HYDROLOGY AND CONTAMINANT TRANSPORT ON FLATWOODS WATERSHEDS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
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Field and laboratory investigations were undertaken to assess surface and subsurface water and phosphorus flow characteristics of flatwood watersheds in south-central Florida. The field sites consisted of four dairy and beef cattle pastures north of Lake Okeechobee, Florida. Instrumentation for hydrologic data collection included runoff flumes, weather stations, dikes, and an extensive network of shallow monitoring wells. Rhodamine dye, potassium chloride, and potassium bromide were applied as chemical tracers to study ground water movement.

Results of the tracer field experiments showed a strong direct relationship between ground surface slope and runoff flow path. The flat pastures exhibited a large surface flow component as compared to sites with slightly greater slope. Ground water flow, calculated from water budgets, increased as site slope increased. Similarly, ground water velocities, calculated from tracer results, were much higher on sites with greater slope. Concentration of phosphorus in ground water and hydrologic export of phosphorus from the pastures were directly related to land use intensity. Results from these four pasture sites demonstrate that surface runoff constitutes the dominant solute

transport mechanism for the relatively flat sites (less than 0.3% land slope) while ground water flow is the primary transport mechanism on the flatwoods sites with higher slopes.

In addition to the primary phosphorus transport findings, experiments into methodological aspects of hydrologic investigations yielded improved field and laboratory techniques. Screened wells were compared to porous cup samplers for monitoring ground water quality. Extracting ground water samples using monitoring wells was found to have a significant influence on shallow ground water flow. Also, a laboratory method was developed to permit efficient sample preparation of ground water samples where high nitrate levels interfere with ion chromatography detection of bromide tracers. The technique used an enhanced bacterial inoculant derived from lake sediments. The resulting dentrification process successfully removed the nitrate interference without affecting bromide or chloride tracer concentration or detection.

CHAPTER 1
INTRODUCTION

Florida's rapid population and economic growth has forced water resource management to center stage of state political, scientific, and industrial concerns. Now under the spotlight, water managers face pressure to deliver an abundant, high-quality supply of water for a variety of users, including homes, industry, agriculture, and the natural environment. The need for better natural resource management has become acutely apparent in the Kissimmee River/Lake Okeechobee area, where various factors have combined to severely strain regional water resources. Nutrient-laden runoff from agricultural lands north of Lake Okeechobee is one of several contributors to south Florida water quality problems.

The South Florida Water Management District (SFWMD) has reported that high phosphorus concentrations are contributing to the deterioration of water quality in Lake Okeechobee. Much of the phosphorus entering the lake is estimated to be coming from two areas--the Kissimmee River and Taylor Creek/Nubbin Slough basins (Federico et al., 1981). The Kissimmee River Basin Region (KRBR) has undergone extensive agricultural development in recent years, an expansion which is considered to be largely responsible for Lake Okeechobee's water quality problems. State water management officials are currently implementing programs which they hope will reduce this phosphorus runoff problem.

One strategy being pursued is the management of interactions between runoff water and soil. Spodosols, also referred to as flatwoods soils, dominate the KRBR.

These soils are sandy, have a less permeable spodic horizon, and also exhibit a water table which typically rises to the surface during the rainy season. Flatwoods watersheds are usually very flat. This combination of attributes results in a hydrologic system which is difficult to study and quantify. An accurate understanding of the system is, nevertheless, necessary to develop effective and efficient evaluative tools applicable to the south Florida spodosols/flatwoods.

Objectives

The objectives of this study were (1) to document the hydrologic processes affecting contaminant transport in the KRBR, (2) to develop techniques and procedures necessary in the study of these processes, (3) to provide estimates of contaminant transport rates and potentials on typical pasture sites of the area by use of tracer studies, and (4) to relate the hydrologic and contaminant transport characteristics to documented phosphorus concentrations in the ground and surface waters of the investigation sites.

Results will not only assist efforts to understand and control phosphorus transport in spodosols, but will also serve as the basis for analyzing transport of other contaminants and serve as an aid to general water quantity management regulation and design. Any water quality study, contaminant transport experiment, or modeling effort is predicated on the concepts that (1) field data collection and experiment results reflect an accurate assessment of conditions on the site being investigated and (2) results from one site may be combined with models to project conditions at another location subject to different conditions. Thus, in addition to simply generating results for a particular site, experiments must stress first, the integrity of site-specific results and second, the

transferability of these techniques and results. This study strives to address both these points.

The water quality of surface runoff and subsurface flow from flatwoods pastures is largely dependent on the hydrologic traits and idiosyncrasies of the sites. Hydrologic models, both simple and complex, can serve as effective evaluative tools if they are suited to local conditions and if they can be implemented efficiently. As a first step toward quantifying contaminant transport and developing improved agricultural water management models applicable to this area, four beef and dairy pasture sites near Okeechobee were instrumented for hydrologic data collection. A series of related investigations were performed on these sites and are described in this study. These investigations fall into three general areas: hydrologic, contaminant transport and water quality. The three areas of investigation are outlined below.

Hydrologic Investigations

The hydrologic investigations chapter presents data collection strategies and technologies developed and implemented in the field and laboratory investigations. The results and analysis section will describe the general hydrologic attributes for each site and then focus on traits distinguishing each site. Aspects of hydrologic monitoring and data collection receiving special attention in this report are: topography, hydrologic isolation of the pasture sites, design and installation of runoff measurement flumes, well network design and installation, weather, ground-penetrating radar for determining soil profile characteristics, soil borings to assess deeper boundary conditions, application of tensiometric methods, in-situ infiltration tests, water table profiles and fluctuations,

boundary condition effects, runoff patterns, lateral ground water movement, use of ground water flow meters, and development of water budgets for each site.

Tracer Investigations

The tracer investigations chapter describes the series of tracer studies conducted on each site. Two types of tracers (dye and salt) were applied to portions of the pastures. The vertical and lateral movement of these tracers were measured to determine subsurface water movement rates and the potential for contaminant transport on these sites. Reported results will include those from laboratory analysis conducted on shallow ground water samples extracted using a network of wells on each pasture. Additionally, results of analysis for tracers in water samples extracted from deep subsoil cores will be presented. Specific topics covered in the contaminant transport sections are tracer application and sampling procedures, extraction of soil water samples from core samples, preparation of water samples for tracer analysis, detection of dye tracers, and detection of salt tracers. The measured progression of the tracer plumes are compared to simplified models for advective-dispersive transport. The discussion will also stress relating the tracer movement to topography, soil type, boundary conditions and other attributes of the particular sites.

Ground Water Quality Investigations

The ground water quality chapter presents investigations into the occurrence and distribution of phosphorus in ground water of the pasture sites. The concentration of phosphorus is compared to various characteristics of the pasture sites in an effort to draw generalizations regarding phosphorus occurrence and its relation to topographic,

land use, and hydrologic characteristics. Also addressed in detail is the subject of ground water sampling instrumentation and protocol. Wells and associated sampling procedures are compared to an alternate sampling method, porous cup samplers. The appropriateness of the methods are evaluated relative to the objectives of this study and similar investigations on shallow ground water systems.

CHAPTER 2
SITE DESCRIPTION AND CHARACTERIZATION

The dominant soil class in the Kissimmee River Basin Region is spodosols, commonly referred to as flatwoods. Approximately one-third of Florida is classified as having flatwoods soil types. These are characterized by amorphous materials (organic matter, aluminum and iron oxides) in a subsurface horizon. The specific suborder in Florida is Aquods, referring to areas which are seasonally saturated with water, gently rolling range or woodland. Where drained, these soils can support citrus and other special crops (Brady, 1974). The general topographic classification of flatwoods in Florida are: the Gulf Coast and Atlantic Coast Flatwoods (thermic zone) and the Southern Florida flatwoods (hypothermic zone). Data collection sites for this study lie within the Lower Kissimmee River and Taylor Creek-Nubbin Slough Basins (see Figure 2-1). The predominant soil associations in both basins are the Myakka-Immokalee-Waveland and the Wabasso-Felda-Pompano (Caldwell and Johnson, 1982). Despite the high hydraulic conductivities of these soils (>160 mm/h), drainage is poor unless augmented by extensive ditching. Soil Conservation Service (SCS) hydrologic classification is A/D or B/D, the exact class determined by the effectiveness of drainage improvements at lowering the water table.

Natural vegetation consists primarily of wet prairie grasslands interspersed with strands of pine-palmetto woodlands. In the depressional areas, wetlands species predominate. Land use in the two basins is dominated by improved and unimproved pasture. Transformation from a natural marsh and slough system to agricultural lands

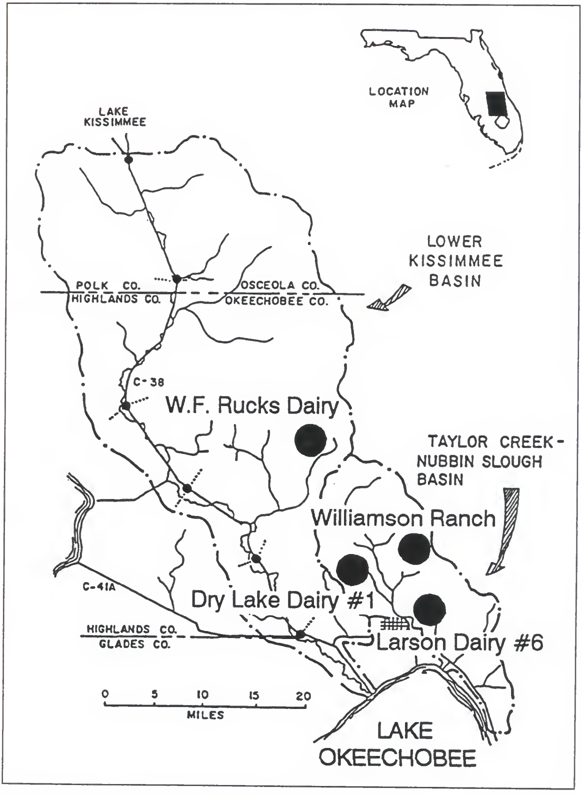

Figure 2-1. Study sites location map.

has been realized through drainage improvements, i.e. ditching. Without extensive ditching and diking, the extremely small watershed slopes (<0.5%) make delineation of watershed boundaries a difficult task.

The following sections provide a physical description and general location of each study site. Included in the site descriptions of each research pasture are maps and diagrams describing topographic features and SCS soils classification. Documentation of site instrumentation systems and other site details are provided in the hydrologic monitorlng sections.

Larson Dairy #6

Figure 2-2 indicates the general location of the Larson site while Figure 2-3 provides a detailed map and topographic survey of the pasture selected for study. The SCS soil survey (USDA-SCS, 1971) indicated that the Larson Dairy #6 site was a moderately well drained Pomello fine sand knoll. The area selected for intensive study was approximately 300 meters from the milking barn directly adjacent to the barn wash treatment lagoons. Mosquito Creek formed one edge of the site. The Larson pasture represented a pasture with atypical topography. An elevation change of 4.5 meters occured from the barn to the creek.

Soil surveys indicated that Pomello fine sands typically have an organic pan at about 106 cm which measures 5 to 15 cm in thickness. The pan is black to dark reddish brown in color. Water tables rise to 75 cm below the surface during the wet season and drop to 190 cm during the dry season.

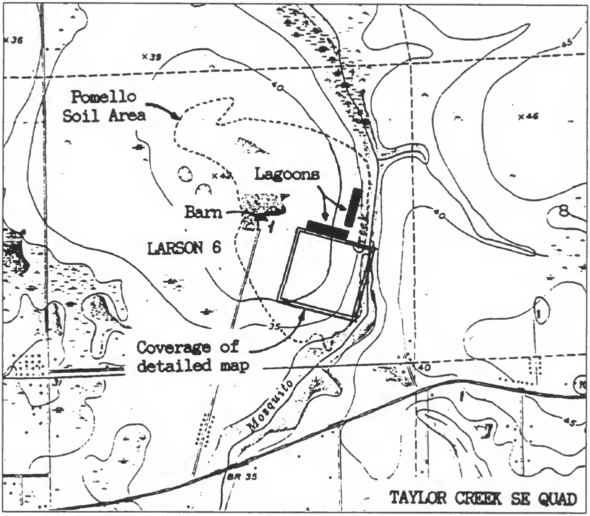

Figure 2-2. Larson Dairy #6 study site location map.

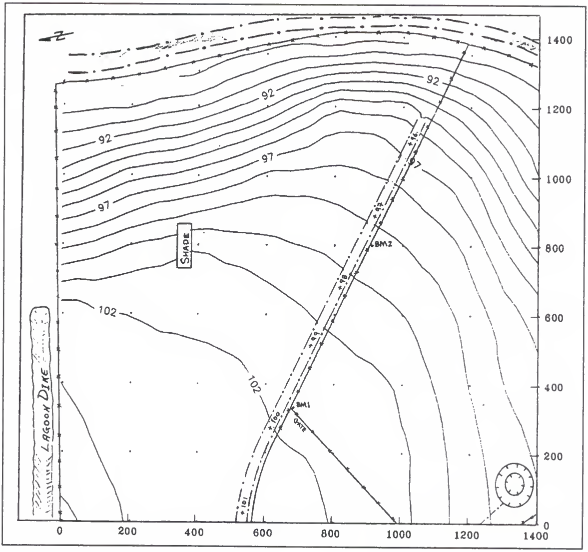

Figure 2-3. Larson Dairy #6 study site topographic map. Vertical and horizontal distances are in feet. Elevations are in feet referenced to a local benchmark assigned an elevation of 100.

W.F. Rucks Dairy

The W.F. Rucks Dairy site, shown in Figure 2-4, was typical of high-quality improved pastures established on Myakka soils. While Myakka was the dominant soil type, soil maps indicated that the northeast corner of the surveyed area fell into an Immokalee zone. A detailed site investigation actually found 6 soil types on the site: Smyrna, Myakka, Immokalee, Punta, Basinger and St. Johns, with Myakka and Smyrna dominating. Myakka and Smyrna fine sands are poorly drained with a well-developed organic pan. The solum thickness for the two soils is typically less than 100 cm for Smyrna and more than 100 cm for Myakka. The W.F. Rucks site was reasonably conducive to field research. Like the Williamson site, livestock density at W.F. Rucks was very much lower than at Dry Lake and Larson. The pasture once served as a tomato field. Much of the row and furrow undulations remained, superimposing a local sinusoidal topographic variation of approximately 30 cm upon the overall 1 meter of fall occurring from the upper portion of the pasture to the ditch. Remnants of shallow drainage ditches also existed and served to facilitate surface drainage off the pasture. These features are apparent in the topographic map (Figure 2-5).

Williamson Cattle Ranch

The Williamson Ranch site, shown in Figure 2-6, was a low-intensity cattle grazing area in the Taylor Creek Basin. Soil survey maps indicated Immokalee and Myakka soils in this area. The site was similar in soil type to the W.F. Rucks and Dry Lake dairies. Unlike the other three sites, trees and palmettos were dispersed through the Williamson Ranch site. A general description of Immokalee soils is given under the Dry Lake Dairy section. The A and E horizons for Myakka are 50 to 75 cm thick. The organic horizon is typically about 15 cm thick, dark reddish-brown in color, strongly acid

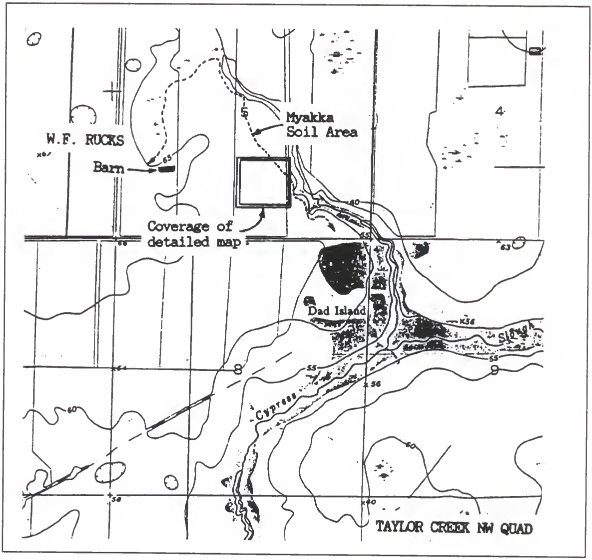

Figure 2-4. W.F. Rucks Dairy study site location map.

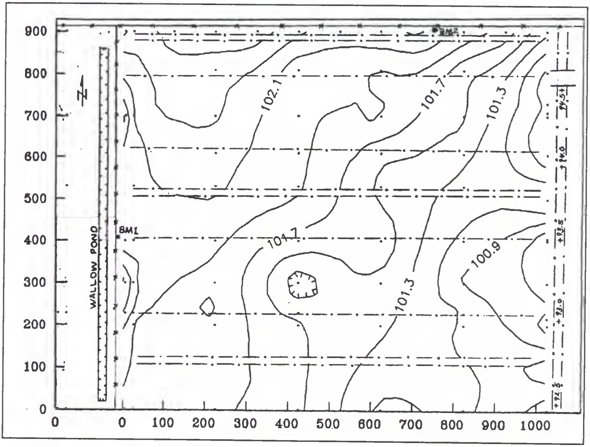

Figure 2-5. W.F. Rucks Dairy study site topographic map. Vertical and horizontal distances are in feet. Elevations are in feet referenced to a local benchmark assigned an elevation of 100.

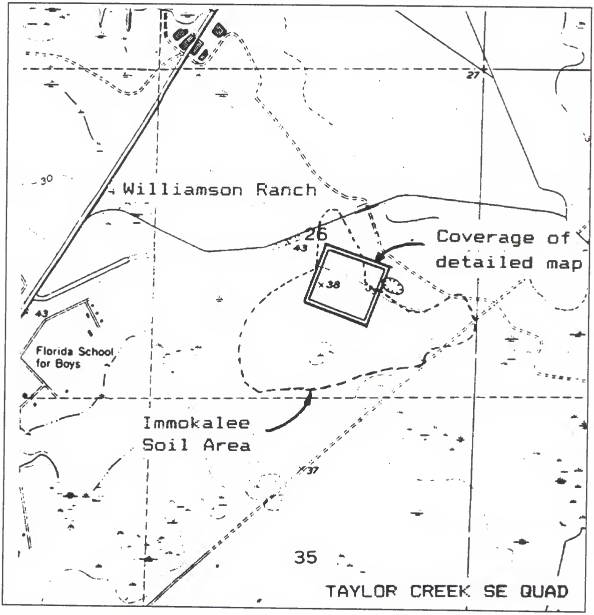

Figure 2-6. Williamson Cattle Ranch study site location map.

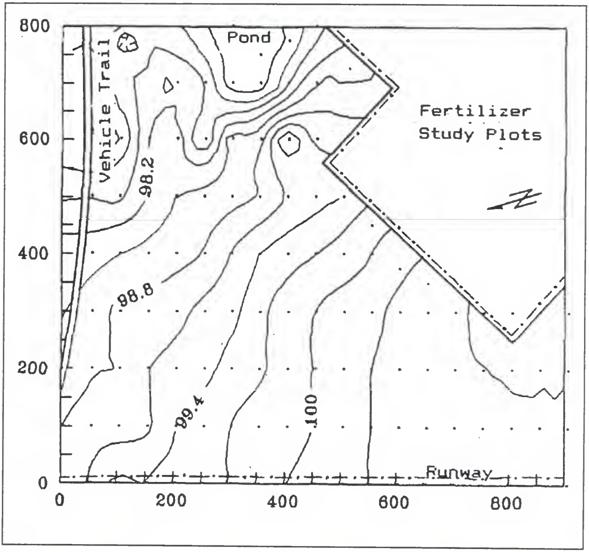

Figure 2-7. Williamson Cattle Ranch study site topographic map. Vertical and horizontal distances are in feet. Elevations are in feet referenced to a local benchmark assigned an elevation of 100.

and weakly cemented. This layer is often highly irregular with many tongues and pockets of white sand. However, on this site the organic pan was unusually uniform and dense, far more dense than at any of the other sites. Immediately below the organic pan was a dark brown layer about 25 cm thick. Normal water table depth for this soil series is 75 cm, varying between 0 and 40 cm during the wet season and dropping below 120 cm during the dry season. The Williamson Cattle Ranch site was by far the most conducive to field research of the four pasture sites. Figure 2-7 provides a topographic map of the Williamson site.

Dry Lake Dairy #1

The Dry Lake Dairy #1 site, shown in Figure 2-8, was situated in an Immokalee fine sand area and was poorly drained. The pasture selected for intensive study was adjacent to a drainage ditch and slough. The Dry Lake site was a difficult location in which to conduct research. Because the site was on Immokalee soil, the pasture became flooded during the rainy season. The organic horizon of an Immokalee fine sand typically occurs at approximately 90 cm and averages 50 cm in thickness. The upper zone of the organic horizon is black and weakly-cemented, while the lower zone is a mottled, dark reddish brown and is even more weakly cemented than the upper layer. During the wet season, the water table stands near or at the surface for short periods and recedes to below 120 cm during the dry season. Figure 2-9 provides a topographic map of the Dry Lake pasture site.

Spodic Horizon Mapping

Perhaps the most defining characteristic of the soil profile and hydrologic regime of these flatwoods sites is the location and integrity of the spodic horizon. The location

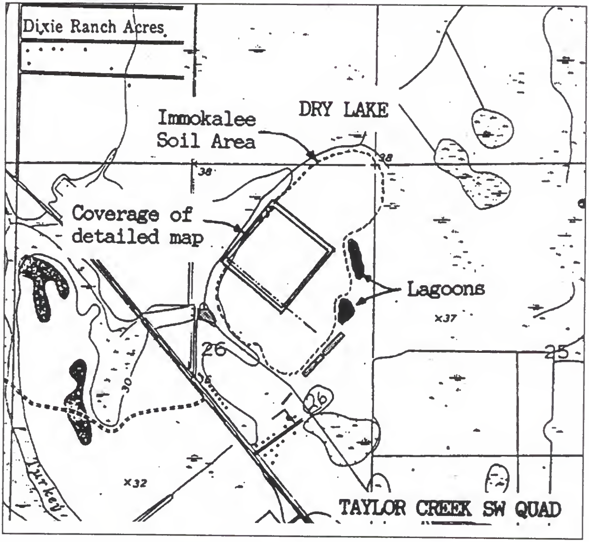

Figure 2-8. Dry Lake Dairy #1 study site location map.

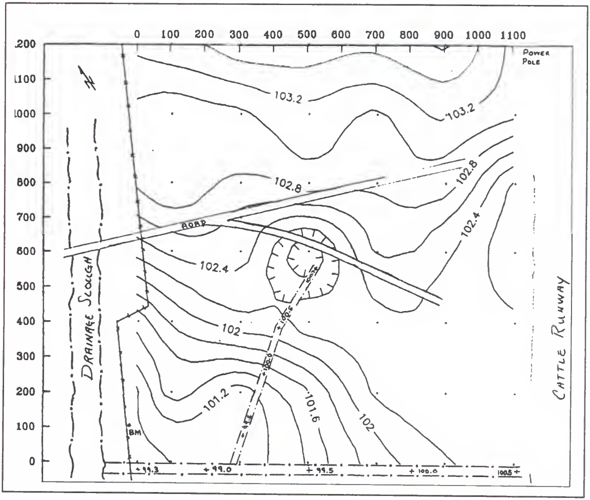

Figure 2-9. Dry Lake Dairy #1 study site topographic map. Vertical and horizontal distances are in feet. Elevations are in feet referenced to a local benchmark assigned an elevation of 100.

of this horizon is indicative of typical water table levels for the site under natural conditions. Normally, identification and mapping of the spodic horizon in the soil profile requires a standard soil survey approach. Ground penetrating radar technology offers an alternative data collection technique to conventional soil surveys. The GPR method was tested on the four pasture sites as part of the hydrologic investigations.

Ground Penetrating Radar Method

While published Soil Conservation Service (SCS) soil surveys are able to provide important information regarding the soil series classification of an area, they are generally not able to provide information regarding soil variability within a soil series. Horizons of a spodosol can have dramatically different physical and chemical properties. Upper horizons are highly permeable and low in chemical sorptive capacity, while the organic pan has extremely high chemical sorptive capacity and low permeability. Knowledge of soil variability is useful for developing input data sets for hydrologic models and for designing effective water and chemical management systems. Determining the occurrence and location of spodosol soil horizons therefore becomes an important task for research into agricultural management practices.

Doolittle (1987) described a ground penetrating radar (GPR) technique which is being used to survey subsurface soil characteristics. The process involves transmitting high frequency (10-1000 MHz), short-duration pulses of energy into the ground from a coupled antenna. The coupled antenna unit is housed in a small box (sled) pulled behind a slow moving vehicle. Most of the instrumentation is carried inside the towing vehicle.

The transmitted energy pulses are partially reflected when they encounter electromagnetic property interfaces in the soil profile. Reflecting interfaces result from

water tables/capillary fringe surfaces, soil horizon changes, and subsurface objects (stones, pipes, etc.). The energy reflected is detected and converted by the receiving unit and recorded on magnetic tape or strip charts. An operator typically walks along side the antenna sled and periodically triggers a device which places a special signal on the recorder. These signals are triggered as the sled crosses preset distance markers. This added information on the charts allows the GPR data to be matched to specific field locations. The GPR strip charts do not constitute a direct measure of any given subsurface feature. Instead the investigator must make a number of soils borings to properly interpret the GPR data.

Field Survey and Data Interpretation

Soil Conservation Service (SCS) personnel from the Sebring, Florida office assisted with GPR surveys and interpretations on each of the four pasture sites. The Sebring office was one of the first four SCS offices in the nation equipped with GPR technology. Two of the other three offices were also in Florida.

The survey was conducted on each site through a series of linear passes along predetermined passes across the pastures as shown in Figures 2-10 through 2-13. Initial interpretations of GPR readings yielded estimates of depth to the spodic horizon for most areas surveyed. However in some areas, the initial interpretations could not determine the location of the spodic horizon within the soil profile. After additional consultations with SCS personnel, final interpretations of the GPR data did yield estimates in these areas. In the process of establishing monitoring well networks on each of the pasture sites, field data on depth to the spodic horizon were also collected. Diagrams of well locations were overlain on contour maps generated from the GPR survey data for each site. In this way, GPR estimates of depth to the spodic horizon

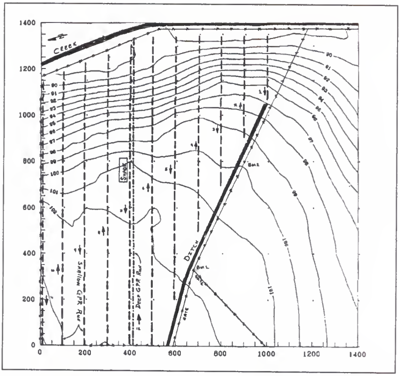

Figure 2-10. Track of the GPR survey on Larson Dairy #6 pasture site.

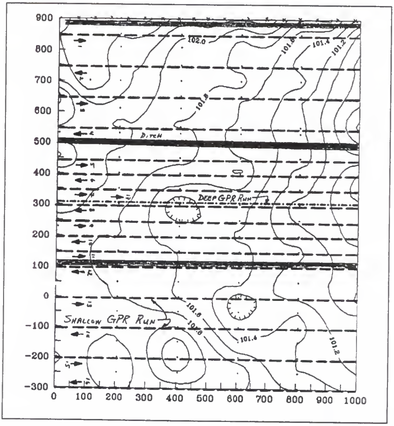

Figure 2-11. Track of the GPR survey on the W.F. Rucks Dairy pasture site.

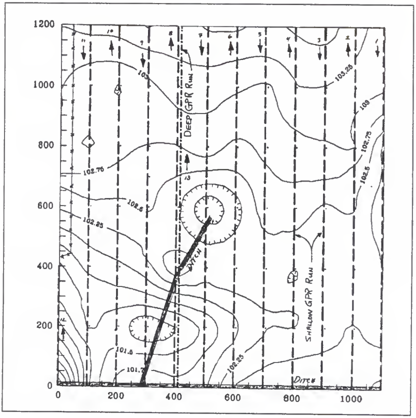

Figure 2-12. Track of the GPR survey of the Dry Lake Dairy #1 pasture site.

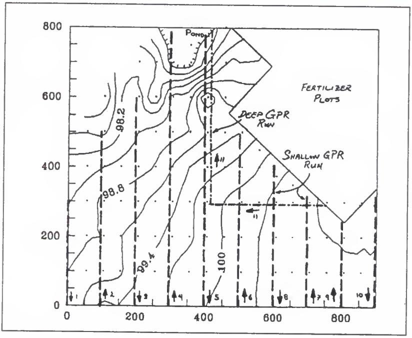

Figure 2-13. Track of the GPR survey of the Williamson Cattle Ranch pasture site.

were determined for each well location. While the direct measurement of spodic depth at the well locations and the GPR estimates both constitute field data, the term "field data" is used in this report to refer to the direct measurements taken at the well locations. This "field data" and the GPR estimates were compared to determine the effectiveness of GPR surveys at estimating the variability of depth to the spodic horizon.

The two spodic depth measurements were compared by determining the "error of estimate" (GPR survey depth - field data depth) for each well location. This is not to imply that there is no error in field data estimates of spodic horizon depths. At the Larson site, for example, field data were collected in some cases by observing color changes in mud lifted by the well drilling auger. Estimates based on such observations are subject to the error inherent in estimating the depth of origin of mud displaced by the drilling auger. This was not a problem at most sites since hand augers were used for installing shallow wells in areas where depth to the spodic was two meters or less.

At one site, Williamson Cattle Ranch, exact depth to the spodic was not recorded during the installation of wells. Instead, shallow wells were installed above the spodic horizon by augering down until the spodic horizon was detected. A well was then installed and the distance between the ground surface and the bottom of the well was recorded at a later time. In establishing wells in this manner, presence of the spodic horizon is assessed at the end of each auger cycle. Thus, it is possible to be a few centimeters into the spodic horizon before detecting its presence. However, such errors were minimal on the Williamson site since the hard organic pan makes its presence immediately known to anyone attempting to auger into it.

Another complicating factor was the point nature of well drilling field observations and the integrating nature of GPR surveys. GPR integrates soil variability

responses over an area having a diameter which increases as interface depth increases. The SCS estimated this effective diameter to be approximately 1.5 meters. Thus in areas of high spodic variability, differences between GPR and point field data may have been the result of actual local soil variability rather than GPR estimation error.

Comparisons with Direct Measurements

For each site investigated several figures provided comparisons of GPR and field data. A general topographic map depicts contours for the ground surface of the pasture and the locations of well stations where field data on depth to the spodic were acquired. A second contour map presents depth to the top of the spodic horizon as determined by the GPR survey. Data point markers are indicated on these spodic surface contour maps and signify specific data points extracted from the continuous GPR response strip charts. Also presented are comparisons of GPR survey results with field data in the form of scatter plots, transect profiles and frequency histograms.

Larson Dairy #6. The SCS soil survey (USDA-SCS, 1971) indicated that the Larson Dairy #6 site was a moderately well drained Pomello fine sand knoll. In the higher elevation portions of this site the observed spodic occurred at depths far greater than the expected 1 meter and deeper even than the published upper limit of Pomello spodic horizon depth (1.5 meters). Field observations ranged from 2.0 to 3.5 meters in this area while GPR estimates were 1.8 to 2.0 meters in the same area. The scatter plot shown in Figure 2-14 presents a comparison of field data determinations and GPR estimates of depth to the spodic surface. The soil profile data along the primary well transect presented in Figure 2-15 shows the underestimation tendency at the higher elevations. The spodic (Bh horizon) in the higher elevations of the Larson pasture was

composed of a coarse sand, dark in color, 30 to 60 cm thick and poorly cemented. Soil above the spodic was composed of white sand.

These observations suggested a Pompano or similar soil series rather than a Pomello. The spodic horizon in the higher elevations of the Larson site probably had a very high conductivity, since the organic accumulation was slight and the sand was observed to be very coarse even in this so-called spodic horizon.

In the lower elevations of the site (Y=300 m to Y=365 m), the Bh horizon was more shallow and typical of a Pomello soil. The spodic occurred at 75 to 150 cm, was black in color and was well cemented. In this area of the pasture, GPR interpretations tended to overestimate depth to the spodic. This appearance of a more typical spodic layer in the profile occurred at the point where the hill began to slope dramatically towards the creek. At the far end of the site (Y>365 m) near the creek, it was impossible to differentiate soil horizons. The soil color was black beginning at the surface and continuing down to at least 3 meters.

Figure 2-16 summarizes the GPR and field observations in the form of a frequency histogram. This representation indicates that while point comparisons of the GPR and field observations do not necessarily match in the 75 to 150 cm range, both data sets exhibit similar frequency distribution in this range. The same is not true for depths greater than 150 cm.

Average error of estimate was -50 cm. Standard error of estimate was 84 cm or 40%. GPR estimates (standard deviation = 36 cm) exhibited much lower variability than did the field observations (standard deviation = 91 cm). Much of the error in the GPR estimates may be due to non-linearity of GPR response characteristics and/or lack of sufficient ground truth data.

W.F. Rucks Dairy. The W.F. Rucks Dairy site was typical of high-quality improved pastures established on Myakka soils. While Myakka was the dominant soil type, soil maps (USDA-SCS, 1971) indicated that the northeast corner of the surveyed area fell into an Immokalee zone. Field data generally agreed with the soil survey characterization and the GPR interpretations. Field data found the Bh horizon to be located at an average depth of 38 cm. The average GPR depth to the Bh horizon was 46 cm. Figure 2-17 shows how the GPR estimates and the field data compare for all data points. Figure 2-18 shows how the two data sets compare along the primary well transect. A tendency toward overestimation is apparent.

Figure 2-19 summarizes the GPR and field observations as a histogram. This comparison shows similar means, but significantly different distribution shapes. The spread of GPR interpretation depths was only a few centimeters while field data exhibited significantly more variability.

Average error of estimate between GPR and measured data was 7 cm. Standard error of estimate was 12 cm or 31%. GPR estimates (standard deviation = 8 cm) exhibited less variability than did the field observations (standard deviation = 13 cm).

GPR survey interpretations indicate a generally uniform organic horizon depth over the site. However a pit excavated to gather soil samples for moisture conductivity analysis showed a highly variable organic horizon within the 120x60x150 cm hole. Many tongues, some up to 25 cm long, were observed in the horizon boundaries. The GPR, on the other hand, integrated horizon interface depths over a larger area -- approximately over a 150 cm diameter region. Small-scale variations (fingers, holes, undulations, etc.) were indiscernible on GPR interpretations. Thus, actual point

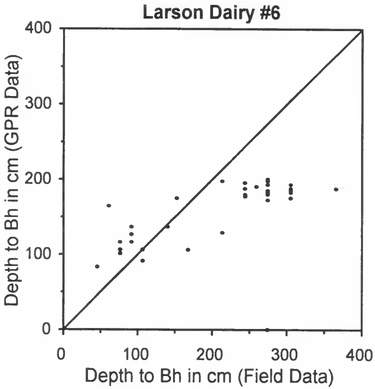

Figure 2-14. Larson Dairy #6 scatter plot comparing ground-penetrating radar (GPR) estimates and field determinations (taken at well locations) of depth to the spodic horizon surface.

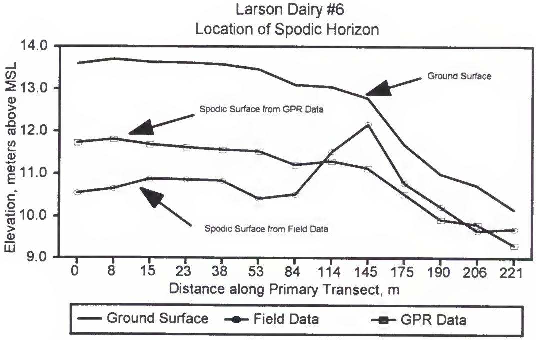

Figure 2-15. Profile section along the Larson Dairy #6 primary well transect showing the location of the spodic horizon surface as determined from ground-penetrating radar (GPR) data and from field data taken at well locations.

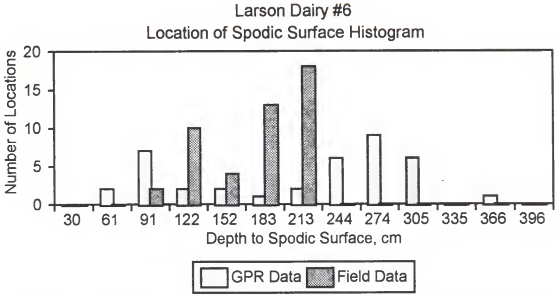

Figure 2-16. Frequency histogram for Larson Dairy #6 depths to the spodic horizon surface as determined from GPR data and from field data taken at well locations.

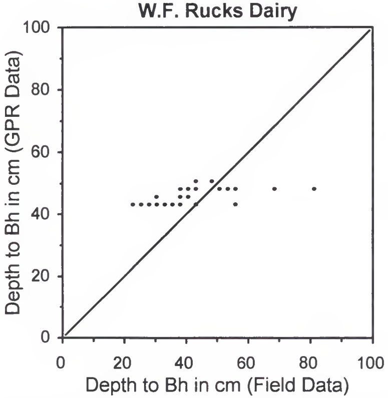

Figure 2-17. W. F. Rucks Dairy scatter plot comparing ground-penetrating radar (GPR) estimates and field determinations (taken at well locations) of depth to the spodic horizon surface.

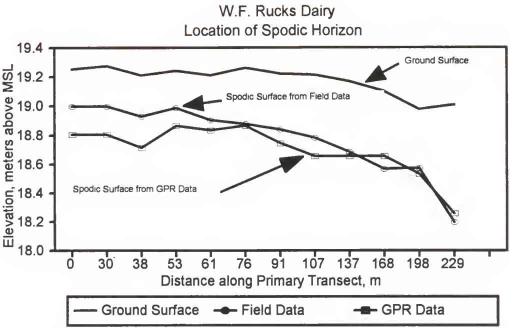

Figure 2-18. Profile section along the W. F. Rucks Dairy primary well transect showing the location of the spodic horizon surface as determined from ground-penetrating radar (GPR) data and from field data taken at well locations.

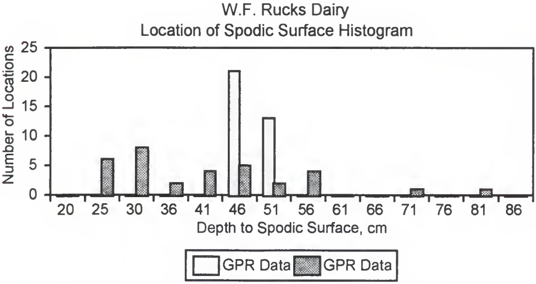

Figure 2-19. Frequency histogram for W. F. Rucks Dairy depths to the spodic horizon surface as determined from GPR data and from field data taken at well locations.

measurements of depth to the spodic may have been less representative on this site as compared to the other three sites.

Williamson Cattle Ranch. Soil survey maps of the Williamson Ranch site (USDA-SCS, 1971) indicate Immokalee and Myakka soils in this area. The site was similar in soil type to the W.F. Rucks and Dry Lake dairies. Unlike the other three sites, trees and palmettos were dispersed through the Williamson Ranch site. A general description of Immokalee soils is given under the Dry Lake Dairy section.

The field data were similar to the soil survey characterization and the GPR interpretations. This spodic horizon was very uniform with few tongues and pockets. It was also much more dense than the spodic observed at the other sites. The permeability was likely to be very low. Field data found the Bh horizon to be located at an average depth of 84 cm. The average GPR interpretation depth to the Bh horizon was also 84 cm. Figure 2-20 shows how the GPR estimates and the field data compare for all data points. Figure 2-21 shows how the two data sets compare along the primary well transect. The GPR survey also indicated a dense layer located at a depth of 3-4 meters. Drilling logs noted an argillic horizon at approximately this depth, or shallower, on most of the site.

Figure 2-22 summarizes the GPR and field observations as a histogram. This representation indicates identical means, but significantly different distribution shapes. The spread of GPR interpretation depths was only a few centimeters while the field data exhibited significantly more variability. GPR interpretations for Williamson may have been complicated by the existence of a water table 15 to 30 cm below the GPR spodic horizon.

Average error of estimate was 0 cm. Standard error of estimate was 20 cm or 23%. GPR estimates (standard deviation = 4 cm) showed much lower variability than did the field observations (standard deviation = 20 cm).

At the upper end of the site (well rows A-H), the spodic's occurrence was very uniform. After this point, it became more shallow, less dense and more variable. By the M and N well rows, the spodic was spotty and very permeable. This observation and interpretation was also supported by water table observations at the site. In the upper end of the site, water table records suggested air entrapment below the spodic resulting in double water table readings in shallow and deeper wells. These dual readings converged to a common value towards the lower end of the site where the spodic was observed to be more poorly defined.

Dry Lake Dairy #1 The Dry Lake Dairy #1 site was situated in an Immokalee fine sand area and was poorly drained. The organic horizon of an Immokalee fine sand typically occurs at approximately 90 cm and averages 50 cm in thickness. Field data agreed with the soil survey characterization (USDA-SCS, 1971), but not with the GPR interpretations. Field data found the Bh horizon to be located at an average depth of 90 cm. The average GPR interpretation depth to the Bh horizon was 68 cm. At some points, ground truth sampling found an argillic horizon at a depth of 1 to 2 meters with a sandy clay loam or loamy sand texture. In areas where this horizon occurred, its depth was substituted for depth to the Bh horizon. Figure 2-23 shows how the GPR estimates and the field data compare for all data points. Figure 2-24 presents similar comparisons along the primary well transect. A clear underestimation tendency is apparent. The frequency histogram comparison of field and GPR data (Figure 2-25) indicates similarly shaped distributions, but significantly different means.

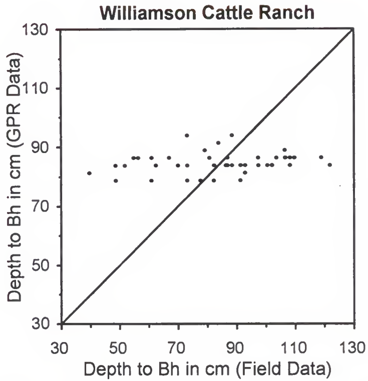

Figure 2-20. Williamson Cattle Ranch scatter plot comparing ground-penetrating radar (GPR) estimates and field determinations (taken at well locations) of depth to the spodic horizon surface.

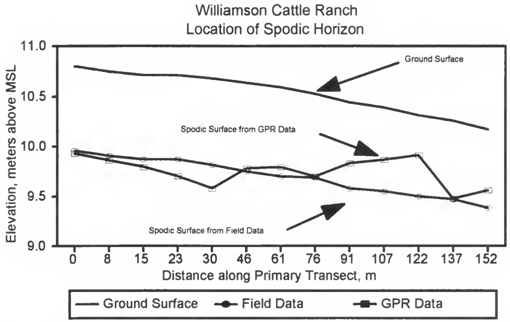

Figure 2-21. Profile section along the Williamson Cattle Ranch primary well transect showing the location of the spodic horizon surface as determined from ground-penetrating radar (GPR) data and from field data taken at well locations.

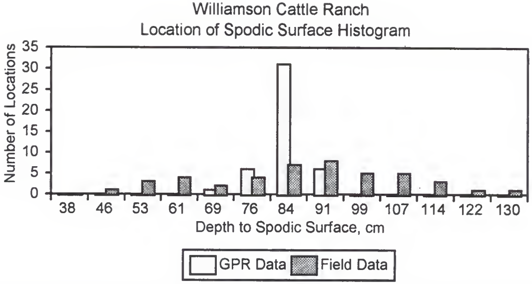

Figure 2-22. Frequency histogram for Williamson Cattle Ranch depths to the spodic horizon surface as determined from GPR data and from field data taken at well locations.

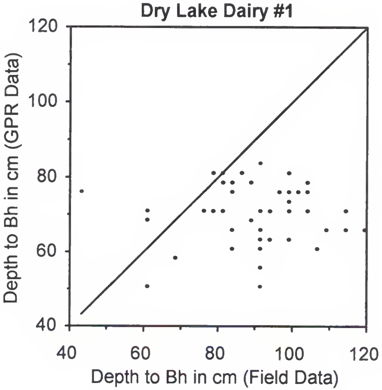

Figure 2-23. Dry Lake Dairy #1 scatter plot comparing ground-penetrating radar (GPR) estimates and field determinations (taken at well locations) of depth to the spodic horizon surface.

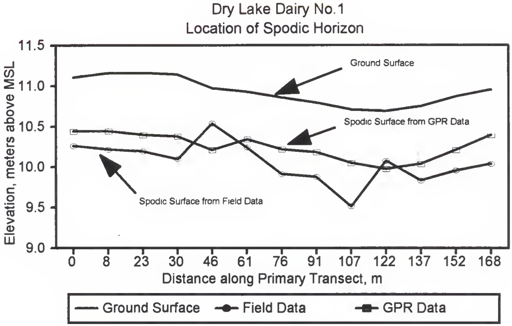

Figure 2-24. Profile section along the Dry Lake Dairy #1 primary well transect showing the location of the spodic horizon surface as determined from ground-penetrating radar (GPR) data and from field data taken at well locations.

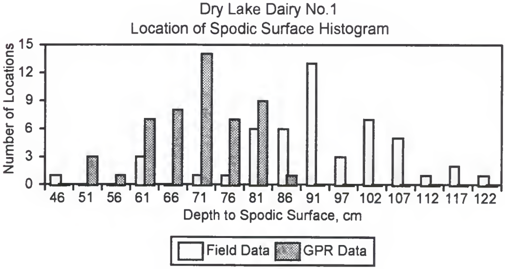

Figure 2-25. Frequency histogram for Dry Lake Dairy #1 depths to the spodic horizon surface as determined from GPR data and from field data taken at well locations.

Interpretations may have been complicated by the indication of a water table 15 to 30 cm below the GPR spodic horizon - a depth approximately equal to that of the actual spodic. Since the water table capillary fringe can yield a GPR echo, the signal attributed to the water table may have been this fringe while the signal interpreted as the water table may have actually been the spodic horizon. Average error of estimate was -20 cm. Standard error of estimate was 28 cm or 30%. GPR estimates (standard deviation = 8 cm) exhibit lower variability than did the field observations (standard deviation = 15 cm).

Method Evaluation

Table 2-1 offers a summary of comparisons between field data and GPR survey estimates for depth to the spodic horizon for each of the four research sites. In general, GPR estimates had significantly lower variance than did the measured depths. This may be partly due to the integrating nature of GPR readings. Overall, GPR tended to underestimate spodic depth. Standard error of estimate ranged from 23% to 40%.

Table 2-1. Summary and comparisons of GPR and field data.

Site	Field Data		GPR Survey		GPR-Field		
	Avg	Std Dev	Avg	Std Dev	Avg	Std Dev	Coef Var
	cm	cm	cm	cm	cm	cm	%
Larson	200	90	160	36	-50	84	40
Dry Lake	90	15	69	8	-20	28	30
Williamson	85	20	84	4	0	20	23
W.F. Rucks	15	13	46	8	7	12	31

The GPR technique tended to perform better in areas where the spodic was relatively uniform (Dry Lake, Rucks and Williamson) than in areas where the spodic

depth varied greatly over the site. It appears that the presence of a water table in the vicinity of the feature of interest may have contributed to the estimation errors observed in this analysis.

Deep Soil Borings

Sampling Method

A series of core samples was taken from two locations at each of the four pasture sites. These borings served several purposes. The first objective was to acquire a physical description of the substratum below the depth inspected during the drilling of the monitoring wells. The second objective was to secure samples for assessing vertical distribution of the salt tracers. The boring and sampling was conducted with the assistance of Agricultural Management Services and Universal Engineering. Samples were taken through a series of two to 150 cm samples from a split barrel sampler hammered into the profile. Total depth of survey was 13 meters. Representative samples were taken from each extracted core and placed in sealed jars and delivered to the field laboratory for inspection and analysis.

Soil Profile Characteristics

Extraction of soil cores from two locations at each of the four sites provided physical descriptions of materials below the soil profile down to a depth of approximately 12.8 meters.

Larson Dairy #6. On the Larson site, a dense floor of shelly sand was present at the bottom of the profile (12 meters). This was found at both the C12 (Figure 2-26) and F1 (Figure 2-27) locations. The layer just above the shell floor was composed of a stiff clay. At approximately 6 meters below ground surface, was a dense horizon of fine

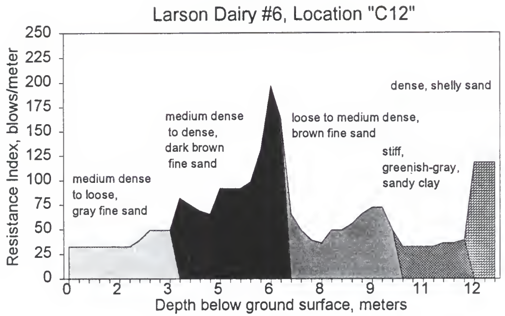

Figure 2-26. Soil core boring profile taken at location C12 on Larson Dairy #6.

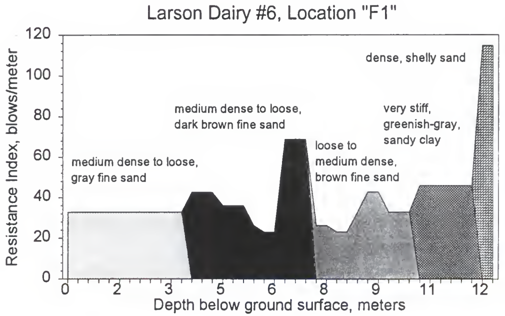

Figure 2-27. Soil core boring profile taken at location F1 on Larson Dairy #6.

sand. This more dense layer was part of a larger horizon of dark material. It was unlear to what extent this material may restrict water movement or at what depth this restriction became significant. Figure 2-26 shows that this may be as shallow as 3.7 meters or as deep as 6 meters. In general, however, two boundary conditions were apparent. First was the dense sand horizon beginning at 1.4 to 6.0 meters. The second began at 10 meters with the clay layer and was reinforced by the dense shell layer at 12 meters. The less dense fine sand layers located above each of these two boundary horizons likely provided the active zone for groundwater movement.

W. F. Rucks Dairy. On the W.F. Rucks site, a dense layer of brown and gray fine sand was found beginning at approximately 8 to 9 meters at both the D7 (Figure 2-28) and E3 (Figure 2-29) locations. Immediately below this layer, a soft silt zone was found which extended to the bottom of the 12 meter boring. Given that this dense bottom portion of the fine sand horizon is underlain by a silt material, the 8 meter mark was a likely boundary condition with most groundwater movement occurring above this depth. The borings at the D7 location showed a dense layer between 2 and 3 meters below the ground surface. The same horizon at the nearby E3 location was not as difficult to penetrate. Another relatively more dense horizon appeared beginning at 4.5 to 5.2 meters.

Williamson Cattle Ranch. On the Williamson site, the floor of the profile was composed of a dense coarse sand beginning at approximately 11 meters below the ground surface at the C15 (Figure 2-30) and D2 (Figure 2-31) locations. However, above this floor, a stiff clay horizon began at 3.7 meters and extended down to approximately 6 meters below the ground surface. Thus, two zones of potential ground water flow were apparent in this profile, one between the ground surface and 3.7

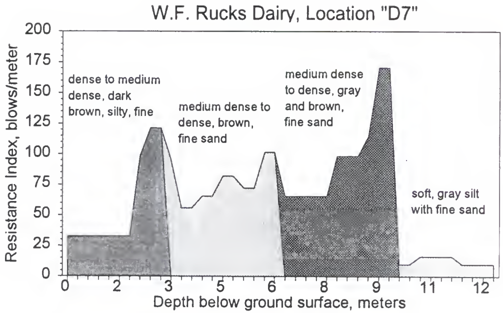

Figure 2-28. Soil core boring profile taken at location D7 on W. F. Rucks Dairy.

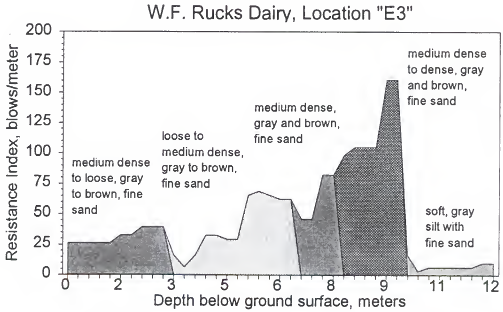

Figure 2-29. Soil core boring profile taken at location D7 on W. F. Rucks Dairy.

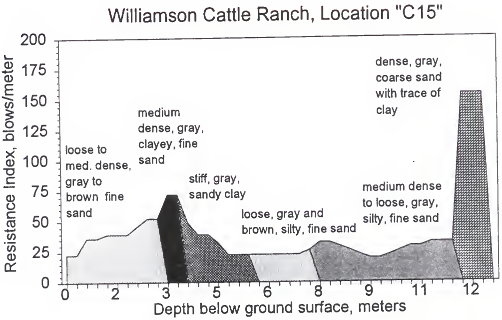

Figure 2-30. Soil core boring profile taken at location C15 on Williamson Cattle Ranch.

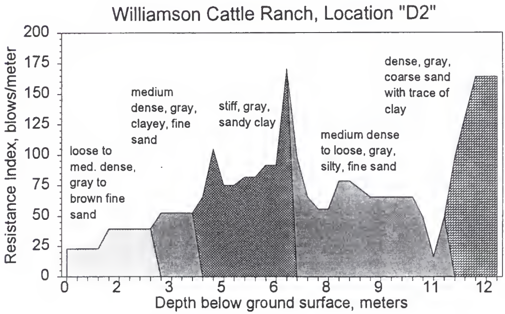

Figure 2-31. Soil core boring profile taken at location D2 on Williamson Cattle Ranch.

meters below, the other between approximately 6 to 12 meters below the ground surface.

Dry Lake Dairy #1. On the Dry Lake site, a clay floor begans at a depth of 10 meters below the ground surface at the D3 (Figure 2-32) and C16 (Figure 2-33) locations. Above this floor were four layers of fine sand of varying density. Between 2.4 and 1.4 meters below the ground surface was a fine sand horizon containing clays at some locations. The extent of the clayey sand over the site and the degree to which this horizon represents an impermeable boundary was unknown.

Method Evaluation

The deep borings into the soil profile were useful in both securing samples for measurement of tracer concentrations and in establishing general soil characteristics and boundary conditions. Most sites exhibited a final floor at approximately 12 meters below the ground surface. This is a critical piece of information for any future modeling effort.

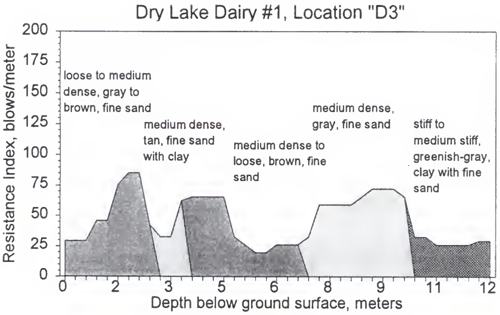

Figure 2-32. Soil core boring profile taken at location D3 on Dry Lake Dairy #1.

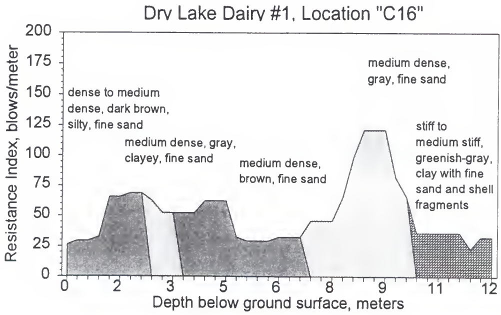

Figure 2-33. Soil core boring profile taken at location C16 on Dry Lake Dairy #1.

CHAPTER 3
HYDROLOGIC INVESTIGATIONS

A series of hydrologic investigations were undertaken in support of various aspects of the overall research project. These investigations included water table fluctuations, ground water flow, weather, surface runoff, and water budget development. This chapter describes the conduct and results of each of these investigations on the study pastures.

Well Network Design and Installation

An extensive ground water monitoring network was established on each of the four research sites. The networks provide an effective means for collecting data on water table gradients, flow vectors, water quality, and tracer movement. The example monitoring well network shown in Figure 3-1 is composed of a tracer application compound, a primary transect of monitoring well stations, and two orthogonal well transects. Each well station was composed of two, three or four wells, depending on the particular location. One of these wells was screened above the spodic horizon while the others were screened below the spodic horizon at varying depths (see Figure 3-2). The W.F. Rucks site represents an exception to this rule, where the shallowness (25 cm) of the spodic horizon made placement of wells above the spodic impractical. Multiple wells at a single station allow the examination of ground water conditions at several different depths.

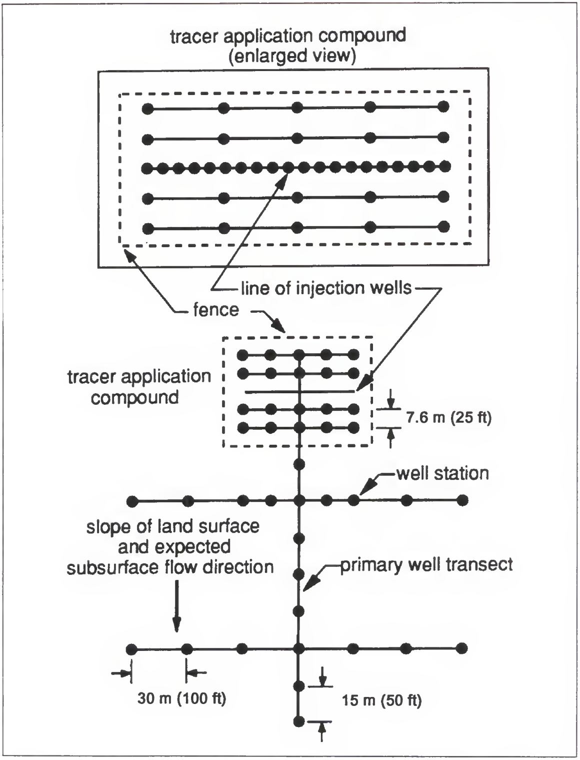

Figure 3-1. Layout of a monitoring well network as installed on each of four research pastures.

The tracer application compound was composed of a line of closely-spaced tracer injection wells and four near-field lines of monitoring well stations. The injection well stations were composed of two wells each: one above-spodic well and one below-spodic well. The density of these wells was high to ensure that any chemical tracer injected into the groundwater would be detectable by the less densely spaced monitoring wells. The closely spaced injection wells effectively constituted a quasi-line-source for subsurface tracer experiments. The entire compound was fenced to prevent interference by livestock and to ensure that no livestock ingest potentially harmful quantities of tracer chemicals--bromide, specifically. Previous tracer studies have reported serious bromide toxicity problems (Owens et al., 1986).

A line of monitoring wells began at the compound and proceeded in the general direction of the surface slope. This line was called the primary well transect. It was expected that this transect will also coincide with the principal groundwater flow direction. However, to insure detection of groundwater gradients and any tracers which may eventually move toward the pasture drainage ditch, the far-field monitoring network was designed to include two additional well transects. These additional transects were positioned orthogonal to the primary transect.

All monitoring wells were constructed of 5 cm schedule 40 PVC pipe and well screen. Some of the wells were screened with PVC pipe slotted using a table saw and wrapped with very fine woven mosquito netting. Shallow wells (those 2 meters or less) were installed using posthole diggers and a bucket soil auger. Those wells deeper than 2 meters were installed using a SIMCO 24000 series hydraulic drilling system equipped with 20 cm hollow stem augers (see Figure 3-3). After drilling, a PVC well casing and screen was inserted into the hollow auger stem and the auger sections were withdrawn. Course sand was poured and packed to a level above the well screen. A layer of

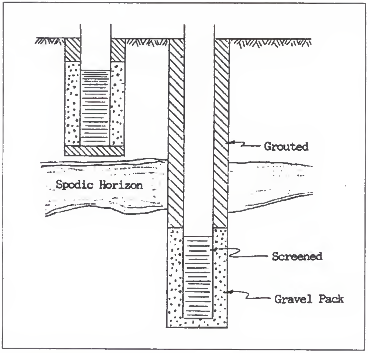

Figure 3-2. Vertical positioning of monitoring wells relative to spodic horizon.

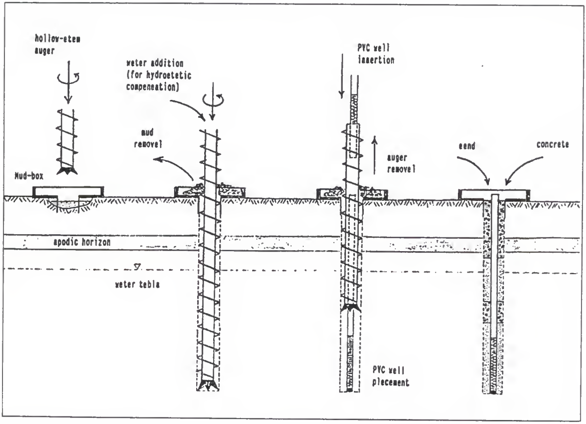

Figure 3-3. Description of the technique used for installing monitoring wells.

concrete isolated the screen section and more sand filled the cavity up to the spodic horizon level. The sand-filled well cavity was also isolated from the soil above the spodic horizon with additional concrete.

One of the primary objectives for establishing the monitoring well network was to collect data on water table levels and gradients over the research sites. Within this objective was the goal of assessing whether the spodic horizon underlying the research sites caused any water table perching. Water level in the wells were measured using a hand-held sensor probe with graduated cable and audio circuit box. In addition to this manual measurement system, several wells were equipped with a continuous water level measurement system. At least two wells per site are equipped with such a system. At some locations, two separate wells (one above-spodic and one below-spodic) at a single station were instrumented for continuous water level measurement. The reason for this duplication was to gain detailed data on the magnitude and duration of water table perching due to the spodic horizon impermeability. In addition to the instrumenting of wells for water level, outflow ditches were instrumented to determine boundary conditions affecting the water table on the pastures at Dry Lake #1 and W.F. Rucks Dairies. The well water level measurement systems consisted of a Druck Model PDCR 830 pressure sensor with fixed-length cable, a junction box, a data cable, and a CR-10 datalogger module (see Figure 3-4).

No automatic subsurface water sampling system was installed on these sites. Instead, a stainless steel, 1-meter bailer and a hand operated diaphragm pump were used to collect ground water samples manually. Half of a sample was filtered in the field and half was left unfiltered. Both filtered and unfiltered samples were immediately refrigerated. Laboratory analyses were conducted to determine soluble reactive phosphorus, total phosphorus, ammonia, nitrate and total nitrogen. Some wells

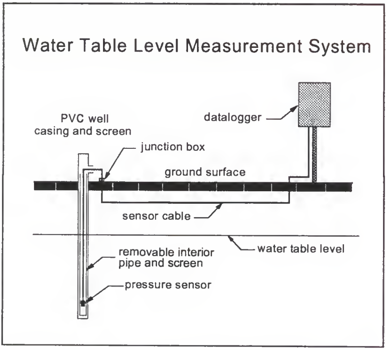

Figure 3-4. Schematic of water level data collection system.

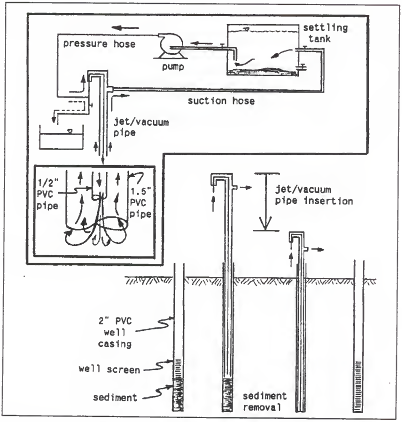

Figure 3-5. Schematic of sediment removal technique.

experienced recurring problems with sediment accumulation. In these cases, wells were cleaned using a jet and suction system shown in Figure 3-5.

Ground Water Flow Meter

Ground water velocity is difficult to quantify because of its low magnitude. A technique was developed by K-V Associates using the measurement of a thermal plume. This company developed a special probe that fits into a 5-cm diameter well. On the probe is a heat source encircled by paired thermistors. The heat source is activated and after a certain amount of time the thermistors are read. A plume is computed from the thermistor readings and shows the direction of the heat and groundwater flow. Before field use, a calibration procedure is conducted in the laboratory using known flow velocities. This calibration yields a reference between instrument reading and the ground water velocity.

The groundwater flow meter method was employed on the monitoring sites to assess ground water flow direction. Proper use of the instrument requires a dedicated technician assigned to calibrate and utilize the device. While some preliminary tests confirmed the groundwater flow direction assumptions for each site, the device could not be used on a regular basis due to its high personnel requirements.

Ground water gradients documented through well level measurements proved to be the only practical indicator of lateral ground water flow patterns on each site. Each site had two orthogonal well transects. This permitted documentation of any lateral components of the gradient vector.

Tensiometric Methods

In addition to monitoring the saturated zone, instruments were installed on each of the four sites to monitor the unsaturated zone. Two sets of tensiometers were installed at each of the four research sites--one set at the weather station and one set at the flume or downslope well station. Each set of tensiometers included tensiometers placed at four depths: 15, 30, 45, and 60 cm. The tensiometer tubes are 2.5 cm PVC pipe attached to a Soil Moisture Corporation 1-bar porous ceramic cup epoxied at one end and acrylic tube at the other end. The acrylic tube and its septum seal are covered by a capped 15 cm long, thin-wall 6.5 cm PVC pipe. This cover sets flush on the top of the PVC coupler and protects the instrument from direct sunlight. The vadose zone soil moisture status is monitored periodically using hand held pressure transducers fitted to a hypodermic needle assembly which were constructed for this project (see Figure 3-6).

In-situ Infiltration Tests

In-situ infiltration tests were attempted at the W.F. Rucks site. This procedure proved impractical given project personnel and equipment resources. The experiment, conducted to procedures presented by Kablan (1986) involved isolation of a 3 meter square area of pasture, instrumentation with tensiometers, and flooding with water trucked in from an external source. A neutron probe system was also employed for determining soil moisture content during the infiltration test. Problems with the tensiometers and particularly with the neutron probe caused the experiment to be terminated. The tensiometer data collected through the course of the investigations proved unreliable. The high maintenance of these instruments exceeded available personnel resources. While data were collected, extensive examination would be required before assigning any certainty to the resulting soil suction values.

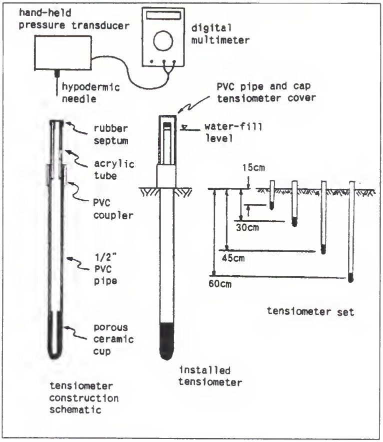

Figure 3-6. Tensiometer design and installation.

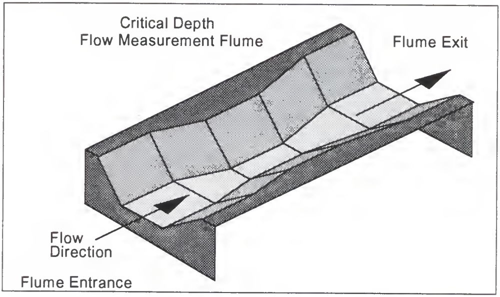

Figure 3-7. Surface runoff flow measurement flume.

Surface Runoff

Collecting accurate surface runoff data from small South Florida catchments is a very difficult task, as previous hydrologic research projects have so clearly demonstrated (SFWMD, 1980). The lessons of previous projects have been applied to the design and installation of the surface runoff measurement systems used in this project. One major problem in runoff measurement is catchment integrity. Surface relief is so small in these areas that it is extremely difficult to define natural surface flow directions and catchment boundaries. Consequently, berms were established around three of the research sites to clearly delineate the collection areas. (The permeability and topography of the fourth site, Larson Dairy #6, was not conducive to standard surface water runoff measurement.) These berms were monitored and maintained to avoid breaches due to livestock traffic.

Another problem was the tendency for measurement system earthworks (ditches, berms, etc.) to modify the hydrologic characteristics of the site, and thus to alter the runoff patterns being measured. Special attention was given to the particular interior and boundary conditions which exist on each pasture. These conditions, if modified, could have altered runoff patterns and the resulting data. Where necessary, however, ditches were blocked, filled or created in an attempt to prevent undesirable conditions such as off-site subsurface inflows and flume backwater problems.

Critical-depth, trapezoidal flumes (see Figure 3-7) were selected as the flow measurement device because they provide accurate measurements and do not significantly modify natural runoff patterns. This class of flume is noted for being highly accurate under free flow (no backwater) as well as submerged flow (significant backwater). In South Florida, submerged flow is not an unusual situation. This is due to the low relief of the catchments and outflow channels. Furthermore, these flumes

are hydrologically unobtrusive because, unlike other flow measurement systems such as drop-culverts and weirs, they do not significantly alter water table levels or surface runoff rates.

The two flumes selected were the Plasti-Fab Trapezoidal Flume Model 12, 45-degree SRCRC, with a design capacity range of 0.0056 to 0.25 cms, and Model 2, 45-degree WSC, with a design capacity range of 8.8e-5 to 0.064 cms. Both were of fiberglass construction. Flume size selection was based on results from previous studies on hydrologically similar research sites (Capece et al., 1987 and 1988). A 24-hour, 5-year design storm, assuming an antecedent water table depth of 43 cm, was used to estimate peak runoff rates for each site. Since results from this previous study have not yet been verified, a conservative SCS runoff coefficient (K=100) was applied rather than the actual value (K=75) indicated by this earlier study. Standard SCS procedures recommend a much higher coefficient (K=300 or K=484). Figure 3-8 presents a schematic of the installed flow measurement systems.

Each system included a trapezoidal flume (with buried cut-off wall), two ultrasonic distance sensors with data cables, and a datalogger module. Concrete aprons provided a transition between the grassed waterways and the flow measurement flume. To avoid the potential for wash-out induced structural failure, 1.2x2.4 meter by 2 cm plywood sheet cut-off walls were fitted and attached to the large flume before placement in the ground. Flumes were placed at a minimum depth into the ground to avoid altering groundwater drainage characteristics. Tops of the flumes were set level to the natural ground surface.

Under free flow conditions, only the flume entrance water depth is required to calculate flow rate. However under submerged conditions, depth measurements at both the entrance and tailwater are required for accurate calculation of flow rate. An

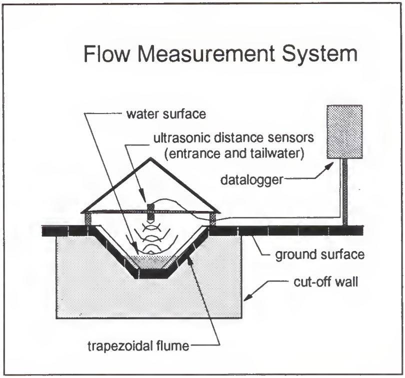

Figure 3-8. Surface runoff data collection system.

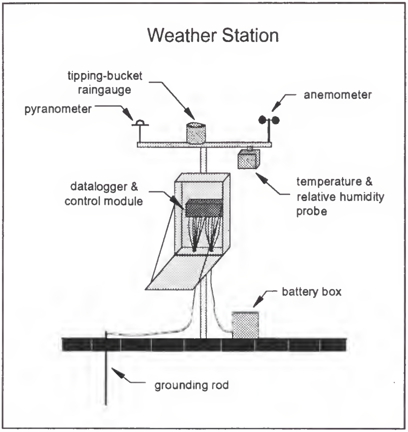

Figure 3-9. Weather data collection system.

Electro Corporation Model PCU Cylindrical Style Ultrasonic Proximity Sensor determined the flume water depth at both the entrance and tailwater. A CR-10 datalogger housed in a shelter received and processed the flow depth data.

Weather Data Instrumentation

Previous research conducted on South Florida small watersheds (Capece et al., 1986) has demonstrated the need for site-specific weather information when developing and evaluating event-based hydrologic models. Because of the irregular distribution and movement of summer convective thunderstorms, rainfall and other weather parameters can vary dramatically over very short distances. This variability directly affects hydrologic variables such as evapotranspiration, water table fluctuations, and surface runoff. Thus, to estimate these hydrologic variables accurately, each of the four research sites was equipped with an automatic weather data collection system, as shown in schematic form in Figure 3-9.

The system was composed of a datalogger/control module and sensors which measured rainfall, wind speed, solar radiation, and temperature/relative humidity. Data stored in the weather station Campbell Scientific CR-10 datalogger were downloaded weekly to a Zenith laptop computer.

Site Instrumentation Summary

Larson Dairy #6

No flow measurement flume was installed on this site. The pasture area was composed of a highly permeable sand with significant surface slope. It was expected that all rainfall will rapidly infiltrate and re-emerge as a seepage zone on the area near the creek. Under moderate to heavy rainfall conditions the creek boundary effectively

merged with the pasture seepage zone into one continuous water body making runoff measurements impractical. Livestock density at this site was high. Figure 3-10 is the symbol key for all site instrumentation figures. Figure 3-11 provides a description of the location of site instrumentation while Figure 3-12 indicates identification codes used for the wells on this site.

A total of 71 well stations were installed on this site. The primary transect was offset from the center row of wells in the compound rather than being aligned with the center well stations. The standard network layout was modified because the curvature of the hill suggested that a groundwater streamline might also curve from the east-southeast direction to the east-northeast direction as it moved down the hill. The primary transect offset provided a better chance to detect any tracer movement along a ground water streamline. A cattle shade structure was located to the north of the primary transect. Unfortunately, the location of this shade structure obstructed the most obvious (and straight) streamline path. Thus, the network established represented a compromise. Supplemental wells were installed at the weather station for continuous water table monitoring.

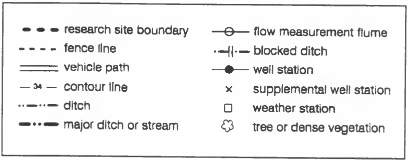

Figure 3-10. Symbols key for site instrumentation maps for pasture figures

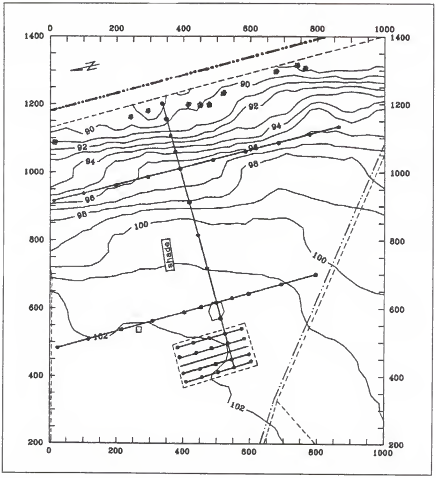

Figure 3-11. Site instrumentation diagram from the Larson Dairy #6 pasture site.

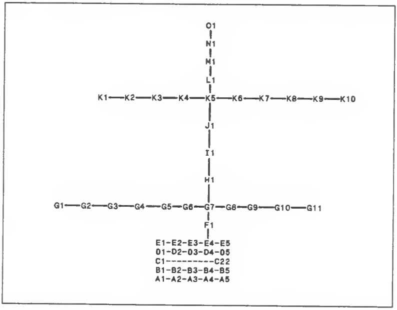

Figure 3-12 Well station identification code diagram for the Larson Dairy #6 pasture site.

W.F. Rucks Dairy

The W.F. Rucks weather station was located approximately 50 meters west of the tracer application compound and the flume station is located approximately 250 meters from the weather station. One well near the weather station and one well at the flume station were instrumented for continuous water table monitoring. Two drainage ditches formed the north and south boundaries of the research site. Each of these ditches had spoil berms on their north and south sides. Originally these berms contained several breaches. These breaches were filled. The continuous berms stood approximately 30 cm above ground surface and were approximately 2 meters across at their base. The total area contained within this berm measured 4.5 hectares. Figure 3-13 provides a description of the location of site instrumentation while Figure 3-14 indicates identification codes used for the wells on this site.

A shallow collection ditch 120 meters in length was constructed at the east edge of the site. This collection ditch measured less than 30 cm deep and was approximately 1 meter wide. This ditch had an accompanying berm on its eastern edge. This berm was less than 30 cm high and is 1 meter wide. The shallow collection ditch discharged into the trapezoidal flow measurement flume, Plasti-Fab Model 2, 45-degree WSC, which had a maximum capacity of 0.06 cms. The flume, in turn, discharged into an existing deep perimeter ditch which flowed into Cypress Slough. Originally the two drainage ditches which form the north and south edges of the site also flowed into this perimeter ditch. These drainage ditches were, however, blocked at four locations along their length and no longer had an outlet into the perimeter ditch. However, two very shallow ditches running the length of the W.F. Rucks site were still capable of carrying flow. Both these ditches emptied into the flow collection ditch leading to the flume.

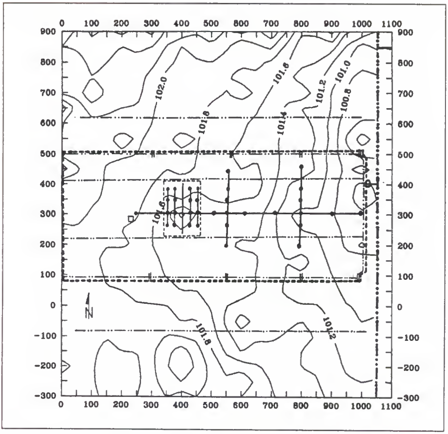

Figure 3-13. Site instrumentation diagram from the W.F. Rucks Dairy pasture site.

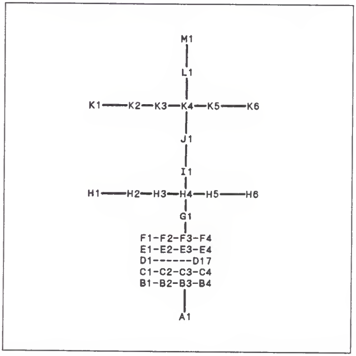

Figure 3-14. Well station identification code diagram for the W.F. Rucks Dairy pasture site.

A total of 51 well stations were established on this site. Unlike the other three research site tracer application compounds, the well lines of this compound had 4, not 5, well stations each. Two shallow drainage ditches formed convenient boundaries for the tracer application compound, thus making this compound more narrow than the others. The W.F. Rucks primary transect and network followed the most probable surface and ground water streamline.

Williamson Cattle Ranch

The Williamson weather station was located approximately 30 meters south of the tracer application compound west corner. The flume station was located approximately 180 meters from the weather station. Three supplemental wells were located at the west corner of the tracer application compound. Two of these wells are instrumented for continuous water table monitoring by the CR-10 datalogger located at the weather station. Two supplemental wells were also constructed at the flume station. One was instrumented for continuous water table monitoring. Figure 3-15 provides a description of the location of site instrumentation while Figure 3-16 indicates identification codes used for the wells on this site.

A small berm isolated the research area from the rest of the pasture. The berm varied in height from 20 to 60 cm above ground surface and was approximately 4 meters across at its base. The total area contained within this berm measured 3.3 hectares. A shallow collection ditch was parallel to this berm for approximately one half of its length nearest the flume station. This collection ditch measured less than 30 cm deep and was approximately 1 meter wide. The shallow collection ditch discharged into the trapezoidal flow measurement flume, Plasti-Fab Model 2, 45-degree WSC, which has a maximum capacity of 0.06 cms. The flume discharged into a newly

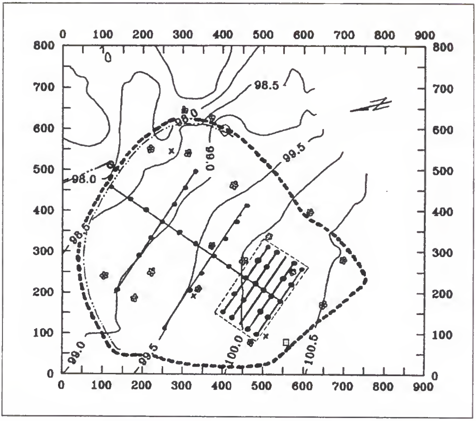

Figure 3-15. Site instrumentation diagram from the Williamson Cattle Ranch pasture site.

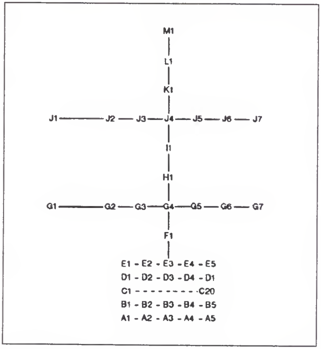

Figure 3-16. Well station identification code diagram for the Williamson Cattle Ranch pasture site.

constructed shallow ditch draining into a small wetland which, in turn, drained into a large ditch leading to Taylor Creek.

A total of 63 well stations were installed on this site. The Williamson primary transect and network follows the most probable surface and ground water streamline. Three additional well stations are located on the Williamson site. These stations are used primarily for collecting water quality samples.

Dry Lake Dairy #1

The topographic characteristics and well network of this site are diagrammed in Figure 3-17. The flume station was located approximately 215 meters from the weather station. Two supplemental wells were constructed at the weather station for continuous water table monitoring. One well near the flume was monitored by the flume CR-10 module.

A low, broad berm isolated the research area from the rest of the pasture. The berm varied in height from 45 to 60 cm above ground surface and was approximately 4.5 meters across at its base. The total area contained within this berm measured 6.8 hectares. A shallow collection ditch was parallel to this berm for approximately one third of its distance nearest the flume station. This V-shaped collection ditch was grassed and measured less than 30 cm deep and is approximately 3 meters wide. The newly constructed collection ditch discharges into a trapezoidal flow measurement flume, Plasti-Fab Model 12, 45-degree SRCRC, which has a maximum capacity of 0.25 cms.

A total of 69 well stations were established on this site. A recently filled ditch was located to the west of the primary well transect. Unfortunately, like the shade structure at Larson, the location of this ditch obstructed the most obvious streamline

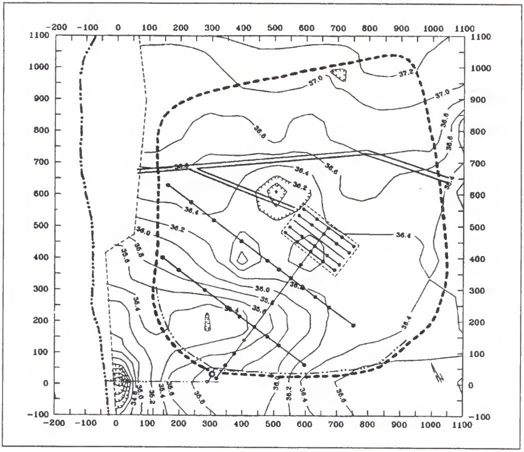

Figure 3-17. Site instrumentation diagram from the Dry Lake Dairy #1 pasture site.

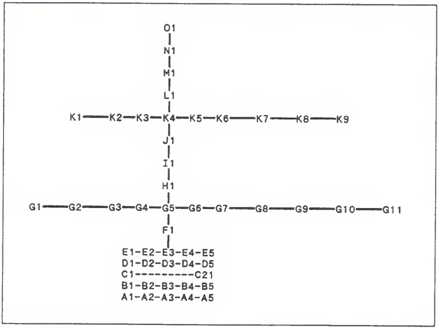

Figure 3-18. Well station identification code diagram for the Dry Lake Dairy #1 pasture site.

path. Thus, the location of the Dry Lake well network represented a compromise. Also like the Larson site, livestock density at Dry Lake was high. Figure 3-17 provides a description of the location of site instrumentation while Figure 3-18 indicates identification codes used for the wells on this site.

Water Table Measurements

Water level elevations were measured at approximately weekly intervals at each pasture site between June of 1989 and December of 1991. These readings permit the assessment of subsurface gradients both along the primary drainage transect and orthogonal to that transect on any given measurement date. Vertical fluctuation of the water table over time can also be inspected for each well location.

Larson Dairy #6

Figure 3-19 presents the water table profile measured on October 3, 1990. This observation represented very wet conditions on the site. The profile was typical for the site in that it exhibited a uniformly sloped water surface between the A and K locations and a dramatic drop in water surface between the K and L locations with a continuing gradient to the O location.

The data show a moderate water table gradient along the G and K row wells, orthogonal to the primary transect. Slopes of the water table along the primary transect and the first orthogonal transect both have an approximate magnitude of 0.5%. This suggests a flow vector not along the primary transect, but rotated 45 degrees clockwise from the primary transect. Inspection of a contour map (Figure 3-20) developed from the water table levels from all the wells along the A through G rows shows a water gradient vector magnitude of 0.5% oriented in the direction from location C1 to

somewhere between locations G6 and G9. This places the actual streamline somewhere between 30 and 60 degrees clockwise from the primary well transect.

The large lateral gradient (orthogonal to the primary transect) was due to two factors, topography and lagoon seepage. The effect of topography can be seen in the slightly sloping ground surface in the G row plot. The rounding of the sand hill, apparent in the general site map of Figure 2-3, caused a drainage effect along the ridge. Also very significant was the effect of the waste treatment lagoon situated adjacent to G1 location. The effect of seepage from this lagoon was quite apparent, particularly between the G1 and G3 locations. The local water table slope between these wells was 1.5%, a fall of 1 meter over a distance of 67 meters.

Along the primary transect, the water table emerged at both the K and O locations. Between the A and J locations, both the above-spodic water table and below-spodic water tables coincide. However beginning at the K location, distinct above-spodic and below spodic piezometric surfaces were apparent. Interestingly, the below-spodic water potential exceeded the above spodic potential and was above the ground surface, indicating artesian conditions and a net upward flux through the spodic horizon.

The interesting water table conditions were the result of a change in the position and integrity of the spodic horizon which occured between the J and L locations. The spodic between the A and J locations was deep and poorly cemented. At the J location the spodic began to resemble regional norms, becoming well cemented and nearer to the ground surface. At this point the surficial system became confined. In addition, a large decrease in water potential occurs between the K and L location. This suggested that a dam effect was taking place at that location. It can be hypothesized that this was

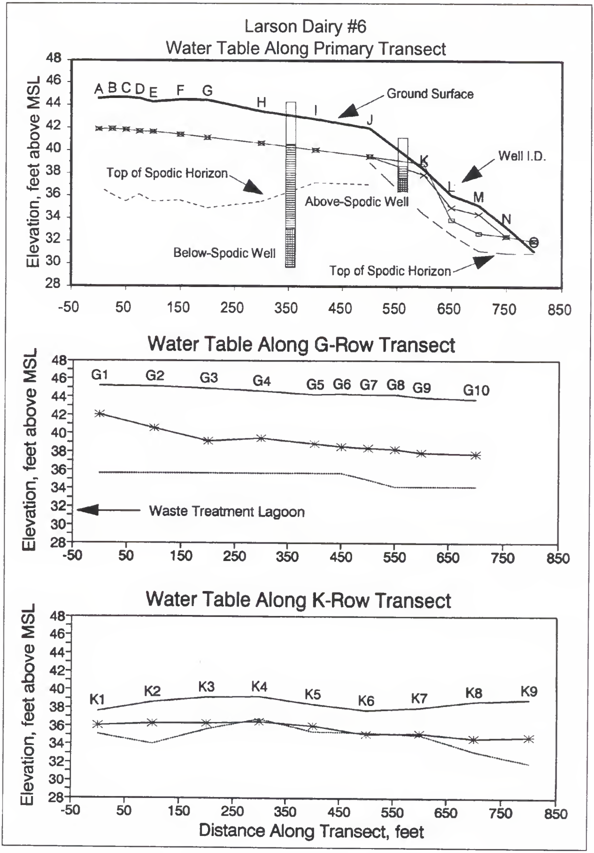

Figure 3-19. Water table profile measured at Larson Dairy #6 on 2/9/90.

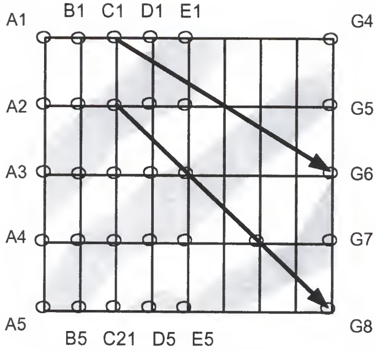

Figure 3-20. Contour map of ground water surface elevation in and near the tracer application compound of Larson Dairy #6 showing direction of gradient.

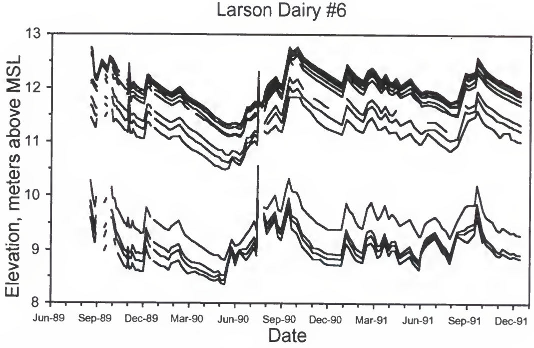

Figure 4-21. Water table surface elevations for all well stations along the primary transect of Larson Dairy #6.

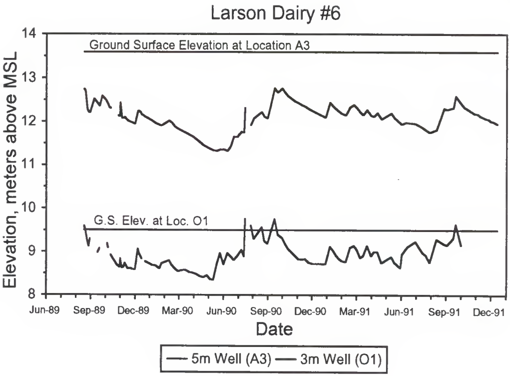

Figure 3-22. Water table surface elevations for wells at the high and low points along the primary transect of Larson Dairy #6.

caused by a lower confining layer at approximately 11 meters MSL intersecting the well-defined spodic which began at the J location.

Figure 3-21 shows the complete period of record for all well locations along the primary transect. At the upslope end of the pasture, the water table never approached nearer than 1 meter from the surface. However at the low end of the pasture near the creek, profile saturation endured throughout the summer and early fall months. This can be seen more distinctly in Figure 3-22 which highlights locations A and O.

W. F. Rucks Dairy

Figure 3-23 presents the water table profile measured on October 30, 1989. This observation represented typical conditions on the site. The profile was representative of data collected at the site. It exhibited a standard drainage curve from the A location at the weather station to the M location near the drainage ditch. The data show no water table gradient along the H and K row wells, orthogonal to the primary transect. This suggested that the actual streamline is aligned coincidental with the primary well transect. Inspection of the contour plot of water table levels near the tracer application compound (Figure 3-24) showed a slight deviation of the streamline from the primary transect. However this deviation was less than 20 degrees. Slope of the water table along the primary transect had a magnitude of 0.2%.

Figure 3-25 shows the complete period of record for all well locations along the primary transect. At the upslope end of the pasture, the water table rose to the ground surface during the summer and fall months. At the low end of the pasture near the ditch, profile saturation occured infrequently and was not prolonged due to the drainage effect of the ditch. This can be seen more distinctly in Figure 3-26 which highlights locations A and M.

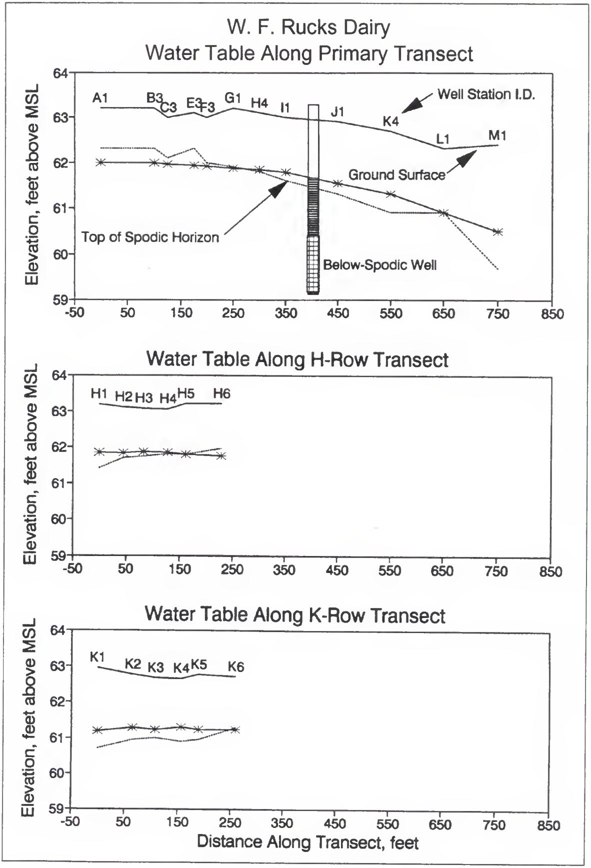

Figure 3-23. Water table profile measured at W. F. Rucks Dairy on 10/30/89.

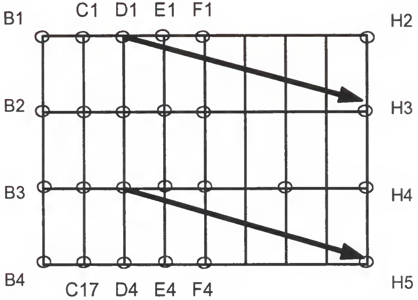

Figure 3-24. Contour map of ground water surface elevation in and near the tracer application compound of W. F. Rucks Dairy showing direction of gradient.

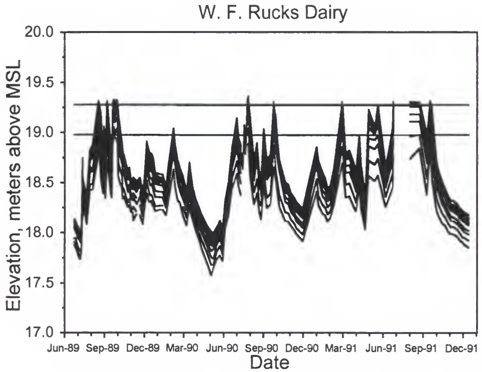

Figure 3-25. Water table surface elevations for all well stations along the primary transect of W. F. Rucks Dairy.

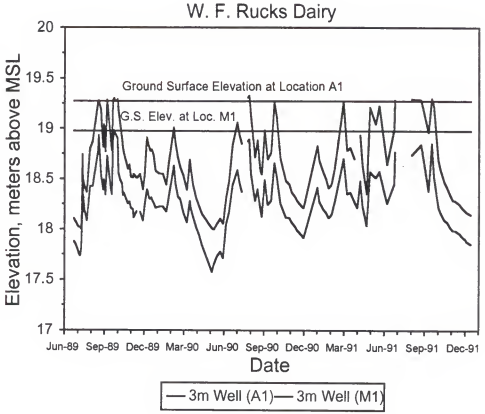

Figure 3-26. Water table surface elevations for wells at the high and low points along the primary transect of W. F. Rucks Dairy.

Williamson Cattle Ranch

Figure 3-27 presents the water table profile measured on October 6, 1989. This observation represented very wet conditions on the site, highlighting the dual water table condition which occured during wet periods. The above-spodic and below-spodic water surfaces merged near the L well location.

The data showed a moderate water table gradient along the G row, orthogonal to the primary transect. The J row wells did not show any significant water surface slope. Slope of the water table along the full length of the primary transect had an approximate magnitude of 0.37%. Along the G row, the water surface slope is 0.2%. This suggested a flow vector not along the primary transect, but rotated counterclockwise. Inspection of a contour map (Figure 3-28) developed from water table levels from all the wells along the A through G rows shows a water gradient of magnitude of 0.4% oriented in the direction from location C10 to G2 or C20 to G5. This placed the actual streamline somewhere between 20 and 40 degrees counterclockwise from the primary well transect.

Figure 3-29 shows the complete period of record for the medium-depth wells at all locations along the primary transect. At the upslope end of the pasture, the deeper water table never approached nearer than 60 cm from the surface. However at the low end of the pasture near the outfall flume and shallow collection ditch, the lower and upper water tables were coincidental. In this area the deeper wells reflected a continuous water table which rose to the surface, albeit infrequently. Despite the low water surface in the deeper wells in the upslope section, profile saturation did occur and was reflected by the shallow well levels. This can be seen distinctly in Figure 3-30 which highlights data from locations A and M. Data for both the above-spodic and below-spodic wells at the A location are presented in this figure. The ability to track

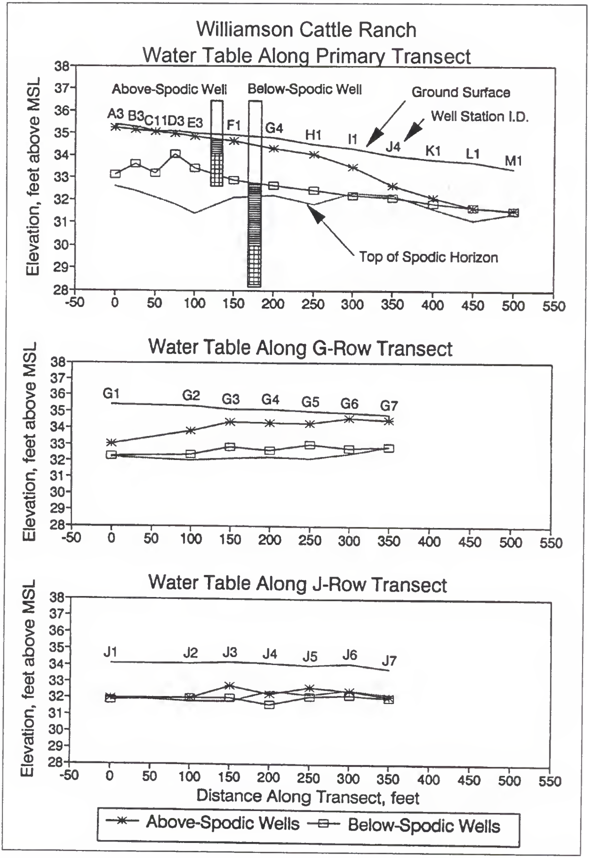

Figure 3-27. Water table profile measured at Williamson Cattle Ranch on 9/6/89.

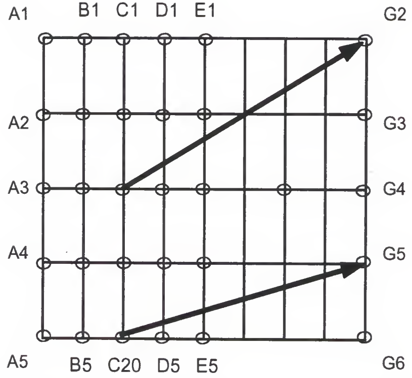

Figure 3-28. Contour map of ground water surface elevation in and near the tracer application compound of Williamson Cattle Ranch showing direction of gradient.

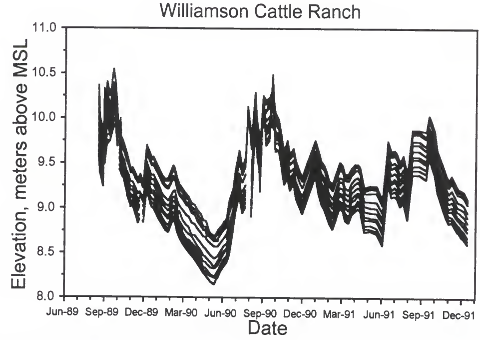

Figure 3-29. Water table surface elevations for all well stations along the primary transect of Williamson Cattle Ranch.

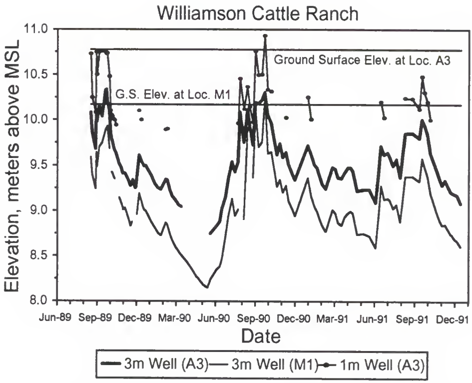

Figure 3-30. Water table surface elevations for wells at the high and low points along the primary transect of Williamson Cattle Ranch.

differences in piezometric surfaces between these two locations was limited by the depth of the shallow wells.

Dry Lake Dairy #1

Figure 3-31 presents the water table profile measured on October 13, 1989. This observation depicted wet conditions on the site with surface ponding evident between the J and M locations. Between the M and O locations the profile drainage effect of the outfall flume and ditch are clear. This drainage effect was impeded from progressing beyond the M location due to an atypical spodic horizon in this section of the pasture. While in most areas of this and the other sites the spodic horizon was composed of accumulations of organic materials, the spodic at the K through M locations was composed of clay, iron and other materials. These materials induce poor drainage conditions in this portion of the pasture and also caused the wells at these locations to act erratically at times when sedimentation and clogging restrict both water entry to and exit from the wells.

Figure 3-31 also shows no sustained water table gradient along the G and K row wells, orthogonal to the primary transect. However the water table along the G row did appear to dip toward location G7 at the center of the row. In the locality of the primary transect the water surface sloped from ponded conditions at the G1 through G3 locations to a low point at G7. This suggested that the actual streamline was aligned slightly clockwise from the primary well transect. Inspection of the contour plot of water table levels near the tracer application compound (Figure 3-32) shows a deviation of the streamline from the primary transect of less than 20 degrees but does reflect conditions for the site during the water table recession periods. Slope of the water

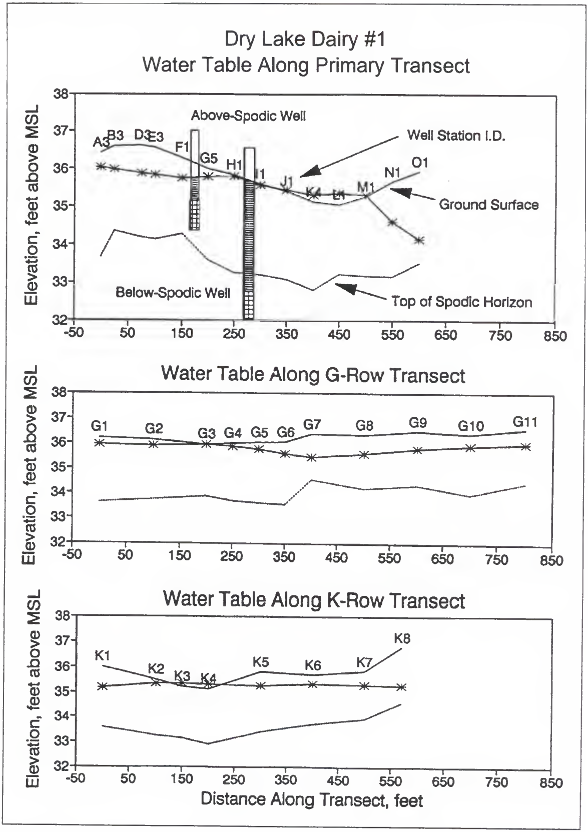

Figure 3-31. Water table profile measured at Dry Lake Dairy #1 on 10/13/89.

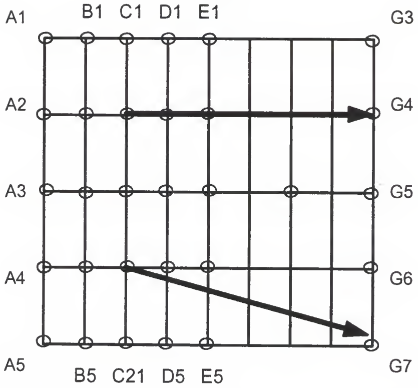

Figure 3-32. Contour map of ground water surface elevation in and near the tracer application compound of Dry Lake Dairy #1 showing direction of gradient.

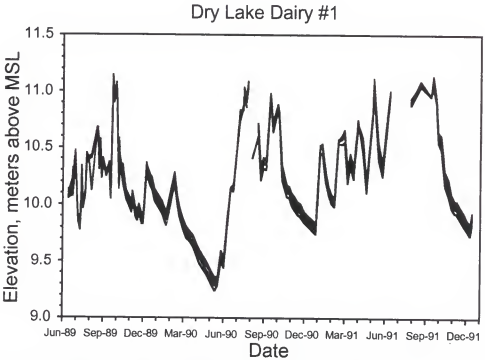

Figure 3-33. Water table surface elevations for all well stations along the primary transect of Dry Lake Dairy #1.

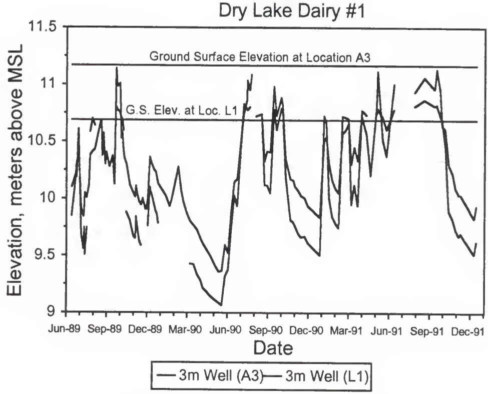

Figure 3-34. Water table surface elevations for wells at the high and low points along the primary transect of Dry Lake Dairy #1.

table along the primary transect had a magnitude of 0.2% which was reflective of gradients observed under a variety of site conditions.

Figure 3-33 shows the complete period of record for all well locations along the primary transect. At the upslope end of the pasture, the water table rose to near the ground surface during the summer and fall months. At the low portion of the pasture, ponded conditions prevailed throughout much of the summer and fall months and were observed even during spring months. This can be seen more distinctly in Figure 3-34 which highlights locations A and L.

Comparison of Results with Well Network Design

Design of the well networks was based on ground slope and the assumed influence of nearby ditches. However, while surface slope was generally a good indicator of groundwater slope, boundary condition effects were not always dominated by the nearest ditch.

Only at the W.F. Rucks site were ground slope, drainage ditches and deeper water body boundary conditions all aligned to create a common gradient effect. In this case, the water table surface profile was well behaved and perfectly sloped. The Larson site was influenced by a crowning ridge and a water treatment lagoon, both of which introduced a significant lateral component to the water table gradient. The water table at the Dry Lake site showed the influence of a nearby drainage slough. Similarly, the Williamson ground water was affected by a deep drainage canal near the pasture.

Nevertheless, in each of these cases, the network established provided an excellent ability to map the ground water profile of the site. The orthogonal transects proved very important to quantifying lateral components of subsurface flow.

Water Budget Results

In developing a water budget for each site, rainfall provides inflows to the system, while evapotranspiration (ET), surface runoff, deep seepage and lateral groundwater flow constitute the system outflows. Rainfall and runoff are components measured directly at each site. In addition to rainfall, each weather station collected data on temperature, solar radiation, relative humidity, and wind speed. These parameters permit the calculation of potential ET using the Penman equation and actual evapotranspiration after introduction of the appropriate crop coefficients. Examples of weather data collected for each site are presented in Figure 3-35. Figure 3-36 presents an example of runoff measurements.

Figure 3-37 through Figure 3-40 provide graphical depictions of daily ET, rainfall, and runoff for each site from April, 1989 to December, 1991. Also included in these figures are water table elevations measured within this period of record. No runoff data is reported for Larson Dairy #6. While seepage faces were apparent near the creek during wet periods, this pasture's water table never reached the surface over most of this site. Therefore, surface water observed at this site was the result of interflow emergence rather than surface flow. Where seepage faces were observed, water often reinfiltrated a short distance downslope from the point of emergence. Both the W.F. Rucks Dairy and the Dry Lake Dairy #1 pastures yielded surface runoff during each wet season, with 1991 being the most active period. At Williamson, surface runoff was measured during only one (1990) of the three wet seasons.

Figure 3-41 and Figure 3-42 allow graphical comparison of monthly rainfall and ET among all sites. Table 3-1 provides monthly totals for rainfall, ET and runoff. Table 3-2 presents annual and total period of record water budget components, including water table storage. Water table storage was not included as a factor in the full period

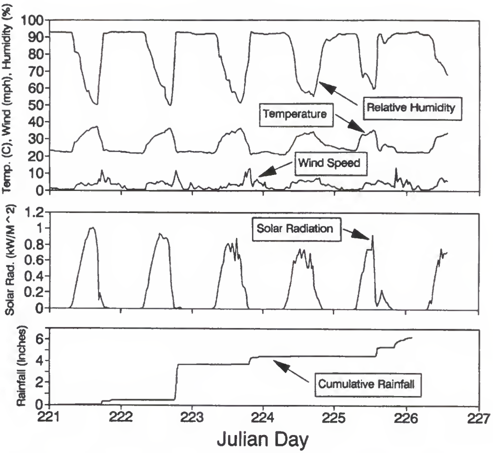

Figure 3-35. Example of weather data as collected at Dry Lake Dairy #1 between 8/9/90 and 8/14/90.

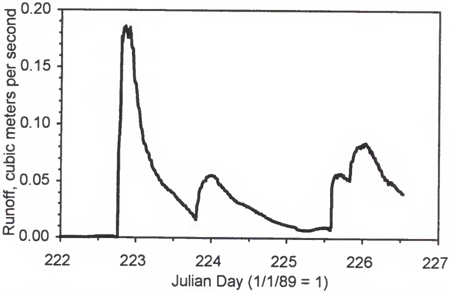

Figure 3-36. Example of runoff data as collected at Dry Lake Dairy #1 between 8/9/90 and 8/14/90.

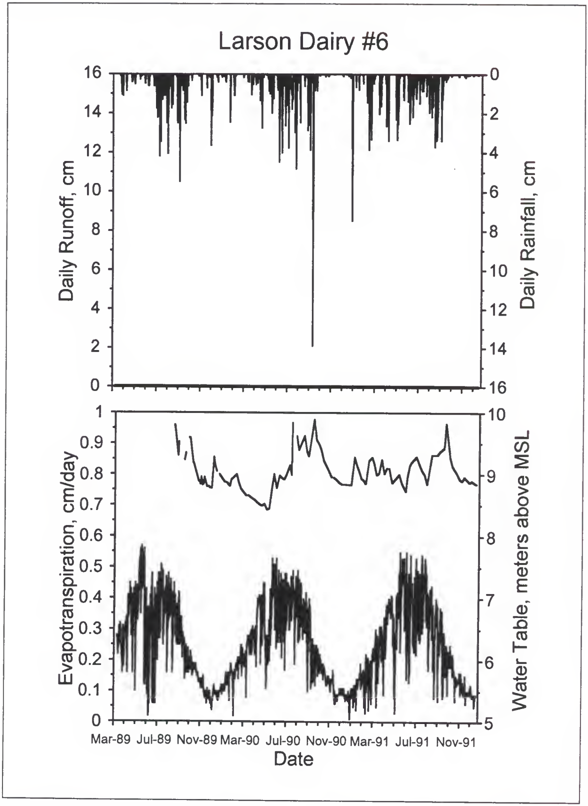

Figure 3-37. Summary of daily evapotranspiration, rainfall, and runoff for Larson Dairy #6. Weekly water table measurements are also presented.

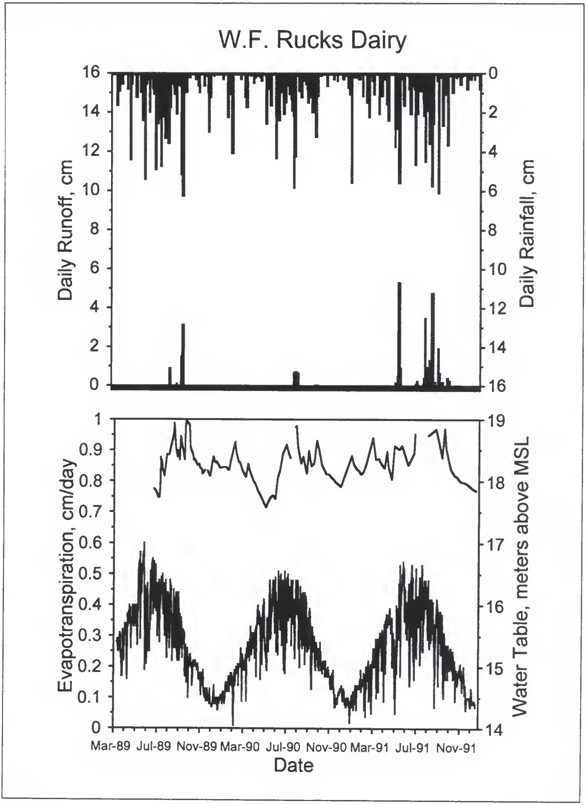

Figure 3-38. Summary of daily evapotranspiration, rainfall, and runoff for W. F. Rucks Dairy. Weekly water table measurements are also presented.

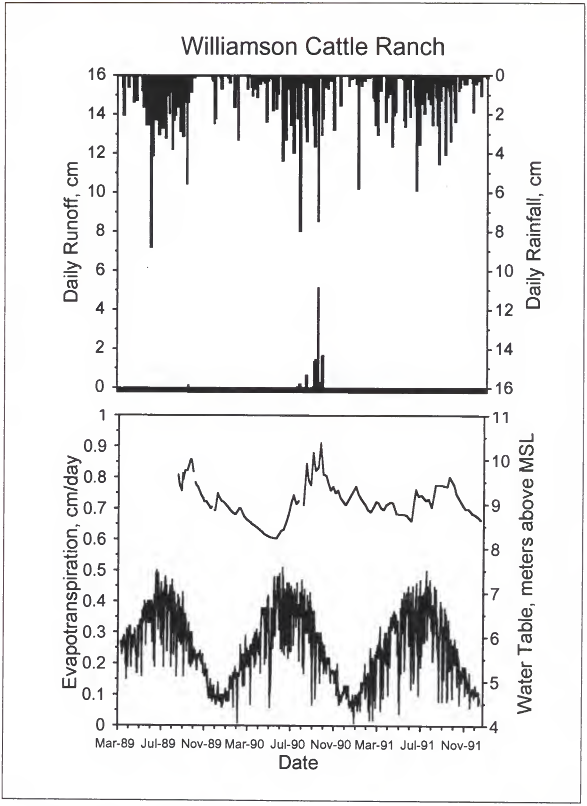

Figure 3-39. Summary of daily evapotranspiration, rainfall, and runoff for Williamson Cattle Ranch. Weekly water table measurements are also presented.

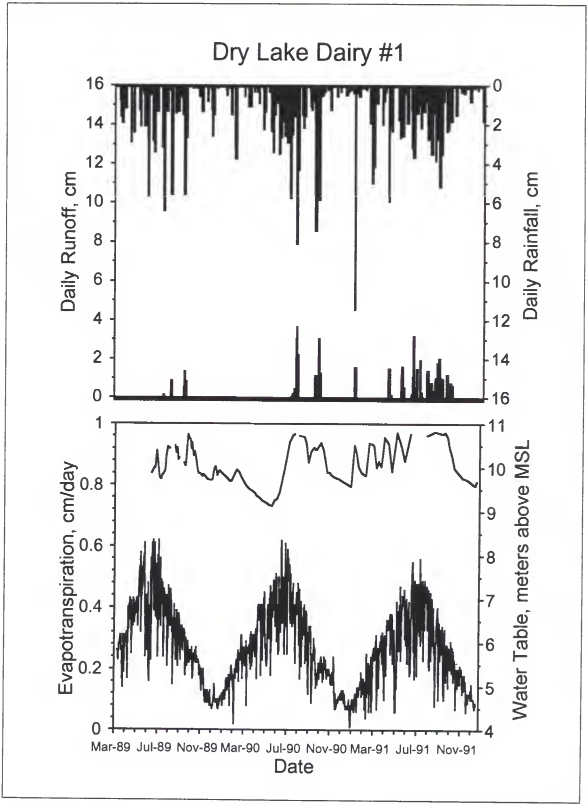

Figure 3-40. Summary of daily evapotranspiration, rainfall, and runoff for Dry Lake Dairy #1. Weekly water table measurements are also presented.

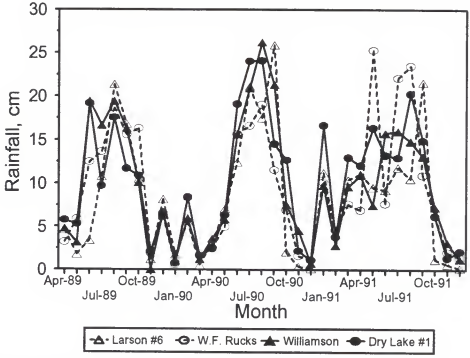

Figure 3-41. Monthly rainfall totals for each pasture site.

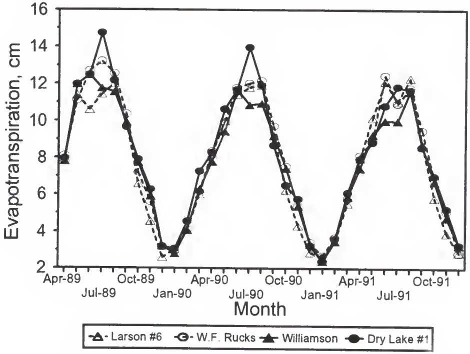

Figure 3-42. Monthly evapotranspiration totals as calculated using the Penman equation and weather data collected at each pasture site..

Table 3-1. Summary of rainfall, evapotranspiration, and runoff for each site. All values are in cm of water.

Month	Larson #6		W.F. Rucks			Williamson			Dry Lake #1		
	Rain	ET	Rain	ET	Runoff	Rain	ET	Runoff	Rain	ET	Runoff
APR-89	5	8	3	8		5	8		6	8	
MAY-89	2	11	6	11		3	12		5	12	
JUN-89	3	11	13	13		19	13		19	13	
JUL-89	11	11	14	13		17	12		10	15	
AUG-89	21	12	19	13		19	12		18	12	
SEP-89	17	10	16	10	2	16	10		12	10	0
OCT-89	11	7	16	7	7	10	8	0.2	11	8	1
NOV-89	1	5	2	6		0	6		2	6	4
DEC-89	8	3	6	3		7	3		7	3	
JAN-90	2	3	1	3		1	3		1	3	
FEB-90	6	4	8	4		6	4		8	5	
MAR-90	1	6	2	6		1	6		2	7	
APR-90	3	8	3	8		4	8		2	8	
MAY-90	7	10	5	10		6	9		6	11	
JUN-90	13	11	16	12		16	12		19	12	
JUL-90	21	12	17	12		21	11		24	14	1
AUG-90	18	12	19	12	7	26	11	1	24	12	13
SEP-90	26	9	12	10		21	9	12	15	9	2
OCT-90	2	6	7	8	0.1	8	7	5	13	7	10
NOV-90	0.4	4	2	5		5	5		2	6	
DEC-90	0.1	3	1	3		1	3		1	3	
JAN-91	11	3	10	3		10	2		17	2	2
FEB-91	4	4	5	4		3	4		4	4	
MAR-91	10	6	8	6		10	6		13	6	
APR-91	11	8	7	8		11	7		12	8	3
MAY-91	10	10	25	9	13	8	9		16	9	5
JUN-91	9	12	8	13		16	10		13	11	5
JUL-91	12	11	22	11	1	16	10		13	12	6
AUG-91	11	12	24	12	19	15	12		20	12	13
SEP-91	22	9	11	10	3	13	9		15	9	9
OCT-91	1	6	6	7	1	7	7		6	7	2
NOV-91	1	4	2	5		3	5		1	5	
DEC-91	0.2	3	2	3		1	3		2	3	

of record calculation due to lack of water table data prior to the summer of 1989. The net column of the table represents the water budget imbalance for each site and accounting period. Most net values were well within reasonable error allowances, however both the Larson and Williamson sites show significant excess water. This net water can be hypothesized as departing the pastures through subsurface flow.

The bar chart of Figure 3-43 presents the net water budget quantity as a measure of potential subsurface discharge. An extra amount of water was added to the Larson net amount for each accounting period. This was done to reflect inflows to the groundwater system from the waste treatment lagoon adjacent to the study pasture. Rough calculations based upon recorded water table data, estimated conductivity values, and assumed area of influence resulted in an estimate of lagoon contribution to the site water budget of 18 cm per year.

While the Williamson and Larson sites consistently exhibit large amounts of excess water, the Rucks and Dry Lake sites show both net surpluses and deficits in their budgets. These small (less than 10 cm) positive or negative values can be attributed to measurement/estimation error, but subsurface inflows/outflows may be the actual cause. Over the entire period of record, Rucks and Dry Lake showed deficits of 5 to 8 cm. If an assumed water table storage was introduced into the water budget calculation for the full period of record (4/89 to 12/31) this would not be likely to balance the water budget. In most cases April water table elevations are below that of December. In some cases the two months may have comparable water table level. However, seldom will an April water table be above a December measurement. Thus, change in water table storage between April, 1989 and December, 1991 can be expected to be positive values of magnitude 0 to 20 cm of water. Including these values in the water budget calculations would increase the deficits observed at the Dry

Table 3-2. Summary of water budget components and the resulting estimation of net water attributable to subsurface discharge from each site. All values are in cm. ET represents evapotranspiration and WT reflects changes in water table storage.

Site	Accounting Period	Water Budget Component in cm				
		Rainfall	ET	Runoff	WT	Net
Larson #6	1990	94	89	0	-3	11
	1991	102	86	0	-5	21
	4/89-12/91	**277**	**251**	**0**	**0**	**26**
W.F. Rucks	1990	91	94	8	-13	2
	1991	130	89	38	-3	6
	4/89-12/91	**312**	**267**	**53**	**0**	**-8**
Williamson	1990	114	89	18	0	7
	1991	112	84	0	-10	38
	4/89-12/91	**323**	**254**	**18**	**0**	**51**
Dry Lake #1	1990	117	96	25	-10	6
	1991	132	86	43	3	0
	4/89-12/91	**340**	**269**	**76**	**0**	**-5**

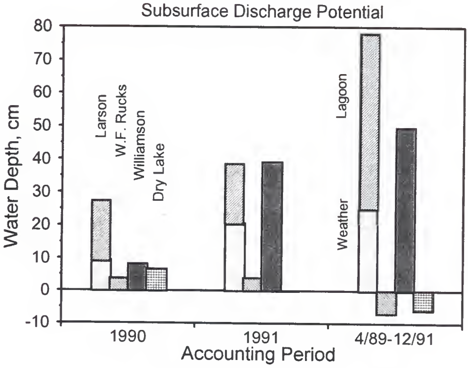

Figure 3-43. Comparison of net water available for subsurface discharge from each site. Values are based upon water budget calculations. For Larson Dairy #6, a "lagoon" component is included based on rough estimates of input to the groundwater system due to leakage from the dairy waste treatment system.

Lake and Rucks sites. The water surpluses of Williamson and Larson would still be above 25 cm after including this storage change assumption. Regardless of the actual magnitude of the surplus or deficit, Figure 3-43 demonstrates a high expectation for subsurface flow at Larson and Williamson and a low expectation for subsurface flow at Dry Lake and Rucks. This water budget evidence matches observed water table gradients for the respective sites: Larson, 1.4%; Williamson, 0.4%; W.F. Rucks, 0.2%; and Dry Lake, 0.2%.

CHAPTER 4
TRACER INVESTIGATIONS

Chemical tracers are a standard method for tracking the movement of surface and subsurface water and solutes. The two types of chemical tracers employed in this study were fluorescent dye (Rhodamine WT) and salt (potassium bromide and potassium chloride). In the salt tracers, the anions (bromide and chloride) served as the actual detection mechanism.

The bromide anion has proven to be an effective tracer of subsurface water movement in a variety of studies (Everts and Kanwar, 1990; Gilley et al., 1990; Butters et al., 1989; and Bathke et al., 1992). In some cases, however, toxicity problems have resulted in the deaths of domestic and wild animals. Bromide applied to the surface of a soil is taken up by plants, particularly when rainfall quantities are insufficient to leach the bromide from the surface zone. If applied with this potential problem in mind, bromide can be used safely. Isolation of direct application areas and testing of nearby and downslope vegetation for bromide content (Abdalla and Lear, 1975) should be part of experimental procedures. Owens et al (1985) documented that a vegetative concentration of 15 gBr/kg dry weight in an area grazed at a rate of 350 cow-days/ha for 3 days resulted in the death of many cows. Where and when vegetative bromide content is not safely below the toxic level, steps will be taken to isolate additional areas from grazing animals.

A variety of other chemical compounds were considered as candidates for use in this tracer study. One group of compounds which has been proven to be faithful

tracers of bromide are the fluorobenzonates (0-TFMBA, PFBA, and 2,6-DFBA). In one respect fluorobenzonates are better tracers of water movement than is bromide -- they have lower diffusion coefficients. One potential problem is that these tracers are acids with pKa values of 3.8, 1.5, and 3.5 , respectively. At pH values near their dissociation constants, increased sorption could result (Bowman, 1984). Bowman used a liquid chromatography method to analyze for these fluorobenzonate anions.

The dye compounds kiton yellow and pyranine (Reynolds, 1966) and Rhodamine WT, sulfo-rhodamine B and lissamine yellow FF (Smettem and Trudgill, 1983) have been shown to be good tracers of water movement. In one study, pyranine was given a lesser recommendation than the others with respect to its conservative properties. Rhodamines have the advantage of being orange dyes which is preferable in soils with high background levels of blue and green color. Water samples from the Suwannee River and fluvic acid extracts from soil both show peak emission in the green range (Smart and Laidlaw, 1977). Rhodamine B dye may prove useful in the studies which call for a highly adsorbed tracer (Kanchanasut and Scotter, 1982). This compound has high affinity for both mineral and organic materials.

While Rhodamine WT is clearly not a tracer of preference for a ground water study, this dye was used for a preliminary experiment to examine vertical movement of water from the ground surface to the shallow ground water. A large quantity of the dye was available from a previous surface water study conducted in the same area. The resulting dye experiment is described in the first section of this chapter. The second section of this chapter describes an experiment into the development of a sample preparation technique necessary for the bromide tracer study. The third section of the chapter describes the actual bromide/chloride tracer study and its results.

Dye Tracer Study

Given the clear limitations of the dye tracer, there was no expectation of tracking the Rhodamine WT dye beyond the immediate area of its application. Nevertheless, the dye tracer experiment was expected to yield information on vertical movement of rainfall from the ground surface to the shallow water table. It was also expected that this experiment would provide an important trial run toward the salt tracer experiments.

Tracer Application

The Rhodamine WT dye tracer was administered to the soil-water system along the center well row of the application compounds (see Figure 4-1). This was accomplished using a small, motorized spray rig modified to fit the purposes of this tracer experiment. The rig was modified to greatly increase the discharge rate using high-volume nozzles and by including an extra pump to drive a side-mounted boom sprayer as a supplement to the existing rear-mounted sprayer. The side spray boom permitted the tracers to be applied directly over the line of monitoring wells. During the actual spraying, the well tops and the surrounding few inches of the ground surface were covered by plastic bags to prevent direct introduction of the tracer into the monitoring wells.

Spray uniformity was evaluated using sampling dishes placed along the target application path. Sampling dishes were placed on each side of the ten-foot spray zone and along the center of the spray zone. The volume of spray solution captured in each dish was measured at the end of the application process. The dye tracers were applied to the sites during the first week of October, 1989. Each site received 40 liters of 20% dye solution diluted into 570 liters of water. This resulting solution was applied to an area of 220 square meters. Total approximate depth of application was 3mm.

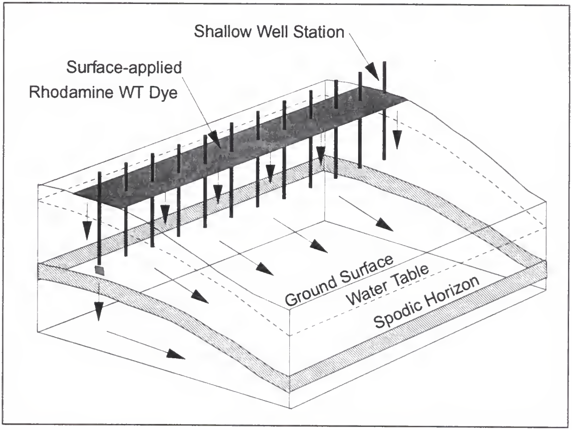

Figure 4-1. Schematic diagram of dye tracer field experiment.

Sampling

No automatic subsurface water sampling system was installed on these sites. Instead, a stainless steel, 1-meter bailer and a hand operated diaphragm pump were used to collect ground water samples. The standard protocol of extracting 3 well volumes prior to sampling was followed in securing ground water for subsequent laboratory analysis. Water extracted from the wells prior to sampling was disposed on the ground surface in the vicinity of the monitoring well introducing problems of recirculation through the soil profile. Frequency of sample extraction varied from every couple of days at the beginning to once a month at the end of the experiment.

The quality assurance/quality control plan developed in association with this project required duplicate well samples, deionized water samples sampled using the same field pumps and bailers (equipment blanks), method reagent blanks, external laboratory matrix spikes, and quality control check standards.

In sampling wells for dye tracers, glass vials were used to store samples prior to analysis in the Okeechobee laboratory. Since only chloride and bromide were of concern in sampling for salt tracers, no special sample preservation was required and samples were stored in 60 ml polypropylene bottles for transport to the Gainesville laboratory for analysis.

Laboratory Analysis

The presence of Rhodamine WT dye in the ground water samples was detected using a fluorometer. The Turner Designs Field Model 10-005 is especially well-suited for rugged applications. The device was set up in the Okeechobee laboratory where all samples associated with the dye tracer study were analyzed.

To initialize the system, it must be set to zero against the background fluorescence, which can be extremely high on these sites. Zeroing is achieved by sampling the naturally occurring water and analyzing it in the fluorometer. A zero setting is automatically made by the system using this background data. The minimum dye concentration that can be read to a certain accuracy is a function of the variation in several background samples. If the required accuracy is within plus or minus 5% (one part in twenty) the minimum concentration of the dye is 20 times the background variability. Maximum concentration of dye is limited only by the ease of measurability as the response curve is non-linear at concentrations above 200 ppb and must be read from a calibration curve (Turner Designs, 1974).

Other considerations for the application of the fluorometer system are the use of the appropriate filters for the dye that is being measured, and loss of the dye to sorption or absorption. Two different sets of filters need to be chosen for the fluorometer (see Table 4-1). Emission filters are used to allow more sensitive measurements by blocking background fluorescence. Excitation filters are used to prevent the inclusion of light from the excitation lamp in the emission spectrum. Necessary filters for a mercury excitation lamp are given below.

Table 4-1. Filter requirements for the analysis of selected fluorescent dyes (Smart and Laidlaw, 1977).

Dye	Excitation Filters Primary Filter	Hg Line nm	Emission Filters Secondary Filter
Rhodamine B/WT	2x1-60+61**	546	4-97 + 3-66

** indicates Kodak Wraten filter, all others are Corning filters

Dye can be lost due to sorption onto sediments that form the streambed surface or onto soil particles when measuring subsurface flow. Other problems can occur from the absorption of dye when using vinyl or rubber tubing, or non-laboratory grade glassware. Minimum detectability in measurement of the Rhodamine family of dyes with this model fluorometer is under 10 parts per trillion.

Dye Tracer Movement

All five well rows within the tracer application compound were monitored during the following three months to document the movement of the dye into the groundwater. The Rhodamine WT dye tracer experiment was inconclusive due to poor tracer performance resulting from dye adsorption to soil particles.

Figures 4-2 through 4-9 show the concentration of dye found in the wells along the center line of the application compound. Each figure shows the mean concentration of samples from all wells along the injection row. Also shown are example measurements from two or three of the wells along the row. Results for other well rows within the compound did not show any evidence of tracer appearance and are therefore omitted.

Even directly beneath the application strip, observation of dye was marginal in most cases. This is apparent in Figure 4-2 and 4-3 which present results from the Larson Dairy site. Apparent changes in concentration measurements wee almost identical in both the shallow and medium depth wells suggesting that the differences in readings wee artifacts of other factors (sample contamination, instrumentation fluctuations, background fluorescence, etc.) and did not portray presence or absence of dye in the ground water samples. Inspection of the other dye concentration figures

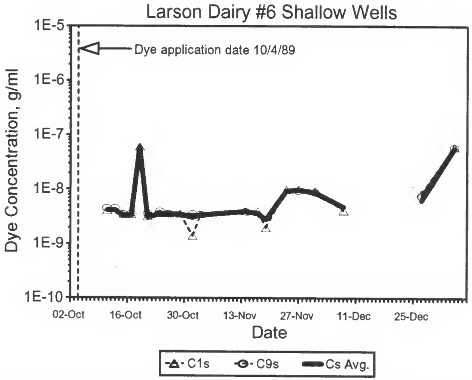

Figure 4-2. Results of Rhodamine dye tracer monitoring in the shallow wells of the injection row (C) at Larson Dairy #6.

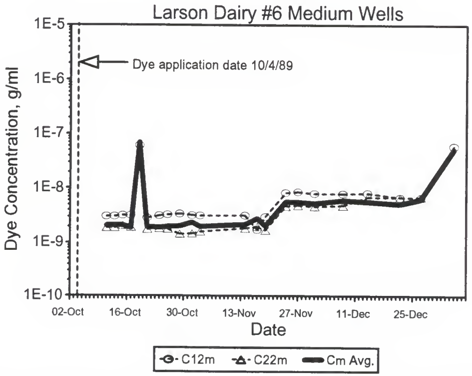

Figure 4-3. Results of Rhodamine dye tracer monitoring in the medium-depth wells of the injection row (C) at Larson Dairy #6.

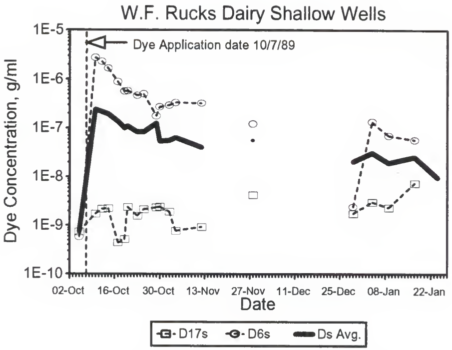

Figure 4-4. Results of Rhodamine dye tracer monitoring in the shallow-depth wells of the injection row (D) at W.F. Rucks Dairy.

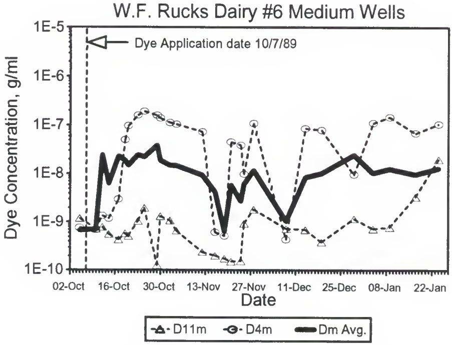

Figure 4-5. Results of Rhodamine dye tracer monitoring in the medium-depth wells of the injection row (D) at W.F. Rucks Dairy #6.

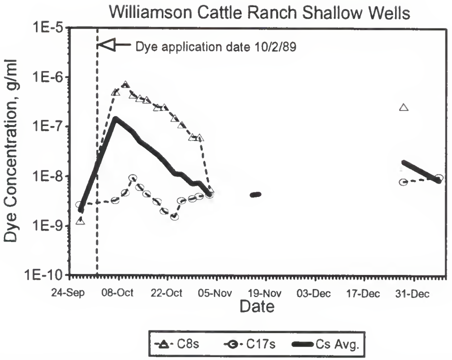

Figure 4-6. Results of Rhodamine dye tracer monitoring in the shallow wells of the injection row (C) at Williamson Cattle Ranch.

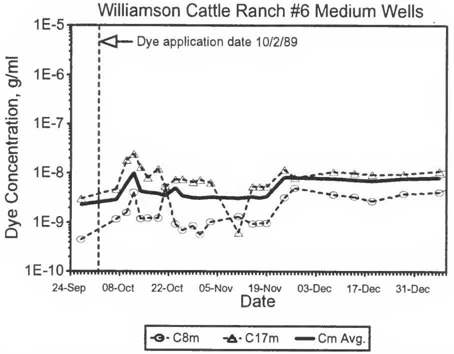

Figure 4-7. Results of Rhodamine dye tracer monitoring in the medium-depth wells of the injection row (C) at Williamson Cattle Ranch.

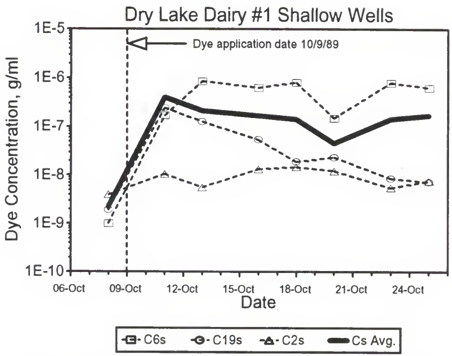

Figure 4-8. Results of Rhodamine dye tracer monitoring in the shallow wells of the injection row (C) at Dry Lake Dairy #1.

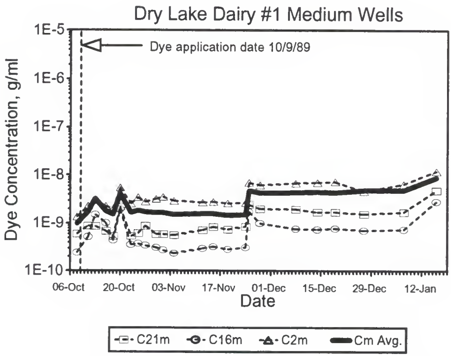

Figure 4-9. Results of Rhodamine dye tracer monitoring in the medium-depth wells of the injection row (C) at Dry Lake Dairy #1.

shows the rather quick appearance of dye in the shallow wells, but very little reliable evidence of appearance in the medium-depth wells.

The dye experiment did provide an opportunity to refine the tracer application equipment and procedures in preparation for the salt tracer experiment. The sampling experience also pointed out the likely problem of tracer recirculation inherent in large-volume sampling from monitoring wells.

Model Comparison

Tracer movement in the vertical direction (from the soil surface or upper horizons to deeper soil horizons) was estimated using the software package CHEMFLO (Nofziger, 1985), a one-dimensional implementation of Richard's equation and the advective-dispersive equation. As a first attempt at estimating the vertical movement of a surface-applied tracer, the software package CHEMFLO was applied to the Immokalee soil example under a hypothetical rainfall scenario.

Before simulating the problem, soil moisture properties again had to be transformed into the particular parameter set required by CHEMFLO. For reasons of simplicity, the Immokalee soil was divided into two generalized horizons, an A/E horizon and a Bh (spodic) horizon. Graphical soil-water properties for the A/E horizon are presented in Figure 4-10 and Figure 4-11.

The necessary input data sets were developed using Lotus 1-2-3 spreadsheets programmed to generate the specific moisture capacity and relative conductivity tables from saturated conductivity and moisture release curves. The method employed to generate these parameters is presented by Campbell (1985) and by Hamlett (1987). This technique fits a power curve to the relationship between soil moisture potential and

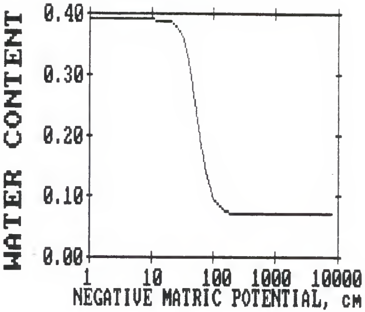

Figure 4-10. Soil-water properties (moisture content vs. matric potential in cm) of an example Immokalee fine sand A/E horizon as used in the Chemflo simulation.

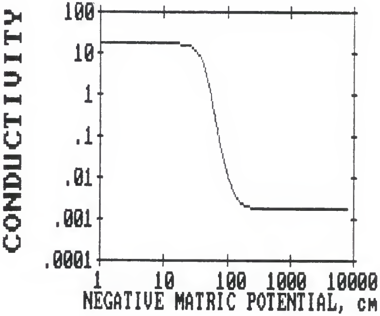

Figure 4-11. Soil-water properties (conductivity in cm/hr vs. matric potential in cm) of an example Immokalee fine sand A/E horizon as used in the Chemflo simulation.

relative moisture content (the ratio of moisture content at a given potential to saturated moisture content) as shown in Equation 4-1.

$$h_m = h_e(\Theta/\Theta_s)^{-b} \qquad [4\text{-}1]$$

where	h_m	=	matric potential,
	h_e	=	air-entry water potential,
	Θ	=	water content,
	Θ_s	=	saturated water content, and
	b	=	empirical parameter.

Using the empirical parameter from Equation 4-1, relative conductivity is then determined by Equation 4-2.

$$K_r(\Theta_r) = \Theta_r^{2+3/b} \qquad [4\text{-}2]$$

where	$K_r(\Theta_r)$	=	the relative conductivity at the relative moisture content (Θ_r=Θ/Θ_s).

The other calculated parameter, specific moisture capacity, is defined as the partial derivative of moisture content (Θ) with respect to soil tension head (h). This quantity is calculated by evaluating the derivative of Equation 4-2. After generating the appropriate soil property parameters, the utility assembles these into tables appropriate for use as input data sets for the simulation model.

The second worksheet was developed to generate soil relative conductivity and specific moisture capacity parameters. The first of these properties are specified through direct entry by the user. Others are calculated using soil properties as typically presented in standard soil characteristics data reports.

Table 4-2 presents soil parameters for an average Immokalee Fine Sand and determined from published Florida soil surveys. Table 4-3 presents a published data set of an Immokalee Fine Sand similar in stratification to that observed at Williamson Cattle Ranch (Soil Science Department, 1984). Table 4-4 represents an idealized Williamson pasture site soil profile and parameters as developed from site observations combined with published data for similar soils. Figure 4-12 presents these Immokalee fine sand profiles in graphical form. The user is allowed to input up to 8 different materials/soils, in this case the eight represent individual soil horizons of a spodosol. Following entry of the moisture release curve data, the curve is displaced for inspection (Figures 4-13) and the user is asked to specify the air entry value of the particular soil material.

After computing relative conductivity and specific moisture content, the worksheet produces output tables for suction head, moisture content, relative conductivity, and specific moisture capacity. Graphical representations of these data, as shown in Figures 4-14 and 4-15, are also created by the worksheet. As well as being useful in this study, these data sets developed for typical Immokalee fine sand soils can find application in other modeling tasks on similar soils.

Using these soil properties, the scenario of a surface applied tracer migrating to above-spodic monitoring wells was modeled by imposing a stable water table at 100 cm below the surface (0 cm matric potential at a depth of 100 cm). Above the water table, only the A/E horizon was assumed to exist. Such a scenario should indicate the fastest rate at which the tracer should be expected to be transported downward under rainy-season conditions. The basis of this statement lies in the accuracy of the assumed boundary condition. A stable water table at 100 cm would allow downward

Table 4-2. Florida average Immokalee Fine Sand soil profile and properties.

Horizon	Depth	Thick	Ksat	Dens.	Water Content (Vol%) at Tension (cm H20)							
	cm	cm	cm/hr	g/cc	3.5	20	30	45	60	80	150	200
A11	0	25	31.6	1.47	42.2	39.1	31.9	19.1	13.4	10.8	7.8	7.1
A12	25	10	32.7	1.55	39.6	37.3	33.9	19.9	12.6	8.7	6.2	5.6
E	35	60	40.7	1.53	38.1	31.9	23.9	14.1	10.1	7.8	5.6	5.2
Bh1	95	15	12.9	1.51	39.7	37.1	35.5	32.1	28.2	25.3	21.4	20.1
Bh2	110	15	11.7	1.45	39.4	35.2	33.2	29.1	24.8	21.6	17.9	16.8
Bh	125	20	6.4	1.51	39.9	37.8	36.3	33.5	30.3	27.2	22.6	21.2
BW	145	30	23.5	1.56	39.3	36.7	34.1	28.4	21.2	13.7	12.7	11.8
C	175		4.1	1.63	35.9	34.4	31.9	28.3	25.3	22.3	19.1	18.1

Table 4-3. Immokalee Fine Sand profile similar to Williamson Cattle Ranch observations (Soil Science Department, 1984).

Horizon	Depth	Thick	Ksat	Dens.	Water Content (Vol%) at Tension (cm H20)							
	cm	cm	cm/hr	g/cc	3.5	20	30	45	60	80	150	200
A11	0	10	35.1	1.41	47.9	42.2	36.2	25.2	20.8	18.4	15.2	14.3
A12	10	13	38.5	1.53	41.1	35.8	28.1	16.4	12.7	10.4	8.1	7.6
E1	23	18	30.9	1.61	36.9	35.4	27.8	16.5	11.4	9.1	6.4	5.8
E2	41	50	37.8	1.64	38.6	33.7	25.1	17.2	10.9	8.2	5.1	4.6
B21H	91	36	0.4	1.64	35.3	34.1	33.6	33.5	33.1	32.1	28.2	26.2
B22H	127	13	2.2	1.64	37.7	36.2	33.7	28.9	26.1	23.6	20.2	19.1
B3	140	35	26.9	1.63	40.1	37.9	33.8	23.6	16.3	12.3	9.2	8.5
C	175		4.1	1.63	35.9	34.4	31.9	28.3	25.3	22.3	19.1	18.1

Table 4-4. Idealized Williamson Cattle Ranch soil profile and properties (Soil Science Department, 1984).

Horizon	Depth	Thick	Ksat	Dens.	Water Content (Vol%) at Tension (cm H20)							
	cm	cm	cm/hr	g/cc	3.5	20	30	45	60	80	150	200
A11	0	25	35	1.47	42.2	39.1	31.9	19.1	13.4	10.8	7.8	7.1
A12	25	10	37	1.55	39.6	37.3	33.9	19.9	12.6	8.7	6.2	5.6
E	35	60	40	1.53	38.1	31.9	23.9	14.1	10.1	7.8	5.6	5.2
Bh1	95	15	0.4	1.51	39.7	37.1	35.5	32.1	28.2	25.3	21.4	20.1
Bh2	110	15	2.2	1.45	39.4	35.2	33.2	29.1	24.8	21.6	17.9	16.8
Bh	125	20	6	1.51	39.9	37.8	36.3	33.5	30.3	27.2	22.6	21.2
BW	145	30	27	1.56	39.3	36.7	34.1	28.4	21.2	13.7	12.7	11.8
C	175		1	1.63	35.9	34.4	31.9	28.3	25.3	22.3	19.1	18.1

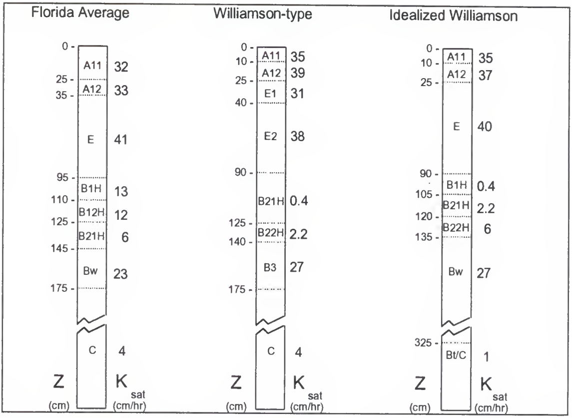

Figure 4-12. Immokalee Fine Sand profile descriptions.

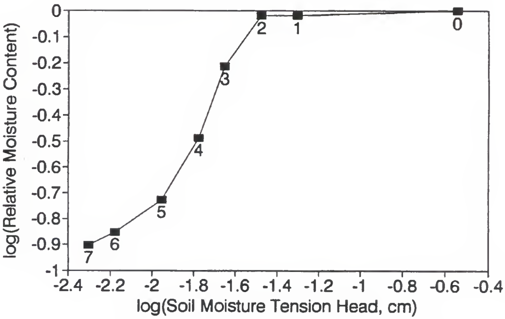

Figure 4-13. Example user prompt screen for designation of air entry value for a soil material. In this case the user would designate point 2 as the air entry value.

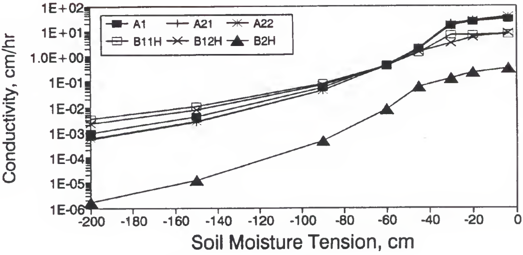

Figure 4-14. Example unsaturated conductivity curve generated by the utility program.

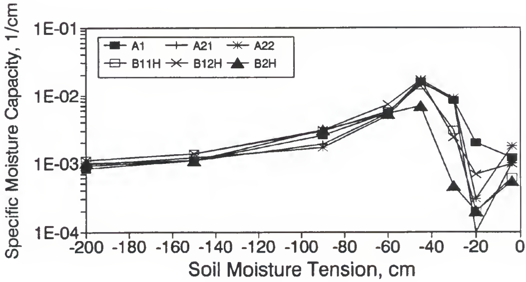

Figure 4-15. Example specific moisture capacity curve generated by the utility program.

water movement much more easily than would a rising water table. Thus, the model results should be interpreted with this in mind.

An initial uniform matric potential of -20 cm was assumed and the model was allowed to stabilize for 24 hours. At this point, a 100 ppm tracer solution was applied to a depth of 2.5 cm. Redistribution was allowed to continue for 72 hours which was followed by two additional rainfall events of 5 cm. After another 24-hour redistribution period a 6-cm rainfall event was applied.

Figures 4-16 and 4-17 present graphical output of the CHEMFLO model at the time of changing boundary conditions. Both the vertical water content and tracer concentration distributions are shown. Figure 4-16 provides a display of cumulative surface water flux (rainfall and tracer solution application) and tracer concentration at a depth of 70 cm as both parameters varied over the 5-day period.

Results indicated that with an application of 2 mm at an initial concentration of 100 ppm, 100 cm wells screened between 50 and 100 cm could be expected to contain 0.5 ppm tracer solutions.

Results from the CHEMFLO simulations were applied in an initial tracer experiment using Rhodamine WT fluorescent dye. Given that background fluorescence of the subsurface water corresponds to a concentration of approximately 4 ppb, the scenario modeled using CHEMFLO was assumed to be sufficient to ensure detection. However, due to the known poor recovery rates of Rhodamine WT dye in a soil environment, the initial concentration was increased by an order of magnitude to 1000 ppm.

Field measurements taken between October and November, 1989, during the Rhodamine WT dye experiment were of marginal value. The length of screening (45 cm) placed so near the ground surface was not suitable for discrete depth sampling.

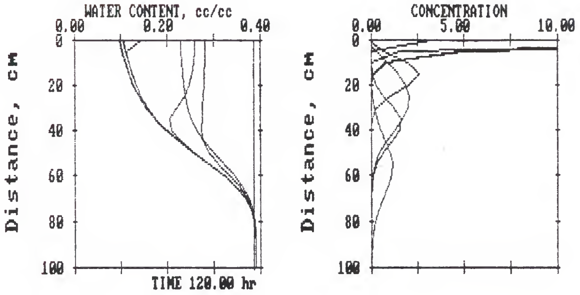

Figure 4-16. Output results showing water content and tracers concentration with depth as produced by the Chemflo simulation using an example Immokalee fine sand A/E horizon.

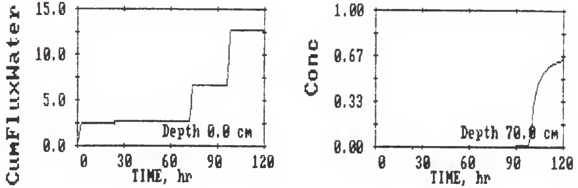

Figure 4-17. Output results showing water flux at the ground suface and tracer concentration at 70 cm depth as produced by the Chemflo simulation using an example Immokalee fine sand A/E horizon.

Furthermore, the dye demonstrated poor persistence in the soil environment. Nevertheless, definite dye concentration peaks were observed in two of the four sites, Rucks and Williamson. During the period immediately following the dye application date, these two sites received the greatest amount of rainfall, 12 and 8 cm inches, respectively. These cumulative rainfall depths are reasonably near the 12 cm depth used in the preliminary model. The other two sites, Larson and Dry Lake , received 7 and 2.5 cm of rain, respectively, during the ten-day period following the dye application date.

Salt Tracers Study

The objective of the bromide and chloride tracer experiments was to measure the shallow ground water flow rate. The chloride tracer was expected to be useful in measuring the movement of water from the surface while the bromide tracer was intended to provide data on the rate of lateral migration of ground water. As a readily adsorbed compound, migration of phosphorus would likely be more attenuated than that of bromide or chloride. Thus, the migration of these anions reflect the movement of ground water rather than the movement of a contaminant such as phosphorus.

Experiment Design

A standard analytical solution to the advective-dispersive equation was applied in an effort to anticipate tracer movement in the shallow ground water from the injection line along the primary well transect. Application of this equation allowed the various design parameters of the tracer experiments to be considered and balanced. The design parameters to be resolved included injection well spacing, monitoring well numbers and spacing, and tracer application mass and concentration.

$$C = \frac{m'}{4\pi t\sqrt{E_x E_y}} e^{-\left(\frac{Y^2}{4tE_y}\right)} \qquad [4\text{-}3]$$

where C	=	concentration
m'	=	tracer mass divided by vertical distribution length
t	=	time after application
Ex	=	longitudinal dispersion coefficient
Ey	=	transverse dispersion coefficient
Y	=	transverse distance from plume center

Equation 4-3 is applicable to a continuous line source problem. The line source is taken to be the vertical shaft of the injection well screen and a reasonable distance below the well screen as might be penetrated by the tracer solution as a result of its "sinking" due to density effects. To consider this line source to be infinite is, of course, an extreme idealization of the actual field conditions. The results of Equation 4-8 provide tracer concentrations at various points along a line orthogonal to the flow direction passing through the center of the plume (see Figure 4-18). This design equation was implemented using the parameters as shown in Table 4-5. Certain parameter values were assumed. Primary among these were values for dispersion coefficients and plume velocity. Varying other parameters such as well spacing and applied tracer mass allowed development of an acceptable experiment design.

This simplified analytical model was applied in a spreadsheet environment. Simulated concentration profiles were generated for multiple tracer plumes originating from the injection row wells. Linear superposition was applied to these plumes to generate a resultant concentration profile (see Figure 4-19).

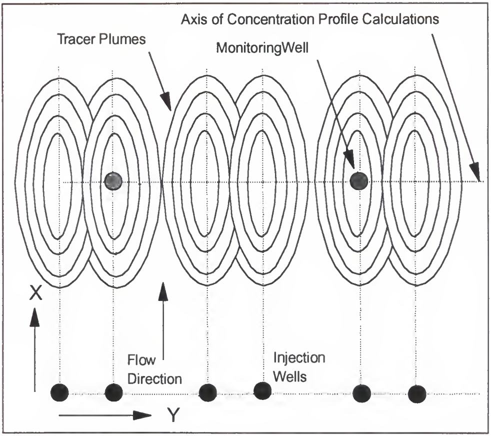

Figure 4-18. Plan view of idealized plume movement and dispersion downslope from injection wells towards monitoring well rows.

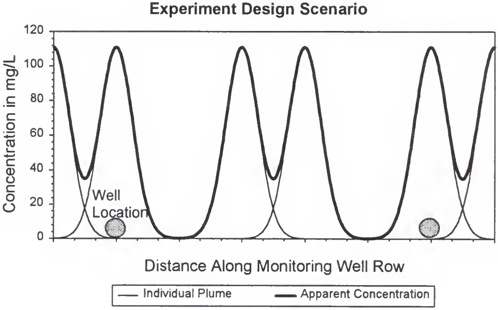

Figure 4-19. Idealized tracer plume concentration profile along the monitoring well row showing superposition of individual plumes generated by each injection well.

Table 4-5. Tracer experiment design parameters generated using an analytical advective-dispersive model for instantaneous line source conditions.

Parameter	Value
Plume Edge Concentration	5 mg/L
Plume Width	300 cm
Tracer Source Vertical Length	200 cm
Plume Velocity	1 cm/hr
Travel Distance	1500 cm
Travel Time	1500 hrs
Longitudinal Dispersivity	10 cm
Transverse Dispersivity	2 cm
Required Tracer Mass per Well	**1-2 kg**

Based upon these calculations and various physical and economic constraints, an injection well spacing of 3 meters was selected. Given this spacing, four lines of monitoring wells were positioned parallel to the injection line 7.5 and 15 meters in both orthogonal directions from the injection line. This compound design provides for 1 to 2 kg of potassium bromide to be applied to each injection well. Given this application mass and the assumed flow field, the analytical equation indicated that bromide would be detectable in the monitoring wells of the tracer application compound and as far as the first orthogonal well transect. Detectability was considered to be concentration of 5 mg/L bromide or greater. Based on these model results, injection quantities of 1500 g KBr (1000 g Br) per well was set for the W.F. Rucks, Dry Lake, and Williamson sites. Due to the likelihood of greater transport potential at the Larson site, an injection quantity of 2900 g KBr (1900 g Br) per well was established for that site.

Tracer solution was not applied to every third well along the injection row to permit use of these wells for monitoring vertical tracer movement along the injection row. Thus, the experiment design did carry a small possibility that monitoring wells

might miss detection of the tracer due to gaps in the plume. However, the model indicated that the extent of the zone below detectable limits was less than 25% as shown in Figure 4-20.

Tracer Application

The potassium chloride was applied using the spray method developed in the dye tracer experiment. Concentrated solutions of potassium chloride were prepared in the laboratory. These solutions were diluted in the sprayer tank using well water from the nearest available dairy/ranch sources. Each site received 100 kg of potassium chloride over 220 square meters. The salt tracers were applied to the W.F. Rucks Dairy and Larson Dairy #6 sites on July 29, 1990. Dry Lake Dairy #1 and Williamson Cattle Ranch were administered salt tracer solutions on July 30, 1990.

The potassium bromide solution was injected into the water table via the shallow (above-spodic) wells along the center row of the application compound. A 500 ml volume of 20% by weight solution was poured into wells each hour during a twelve to fifteen hour period. Every third well location along the injection row was not included in the bromide treatment so that this well could be sampled for tracer presence during the monitoring phase of the experiment. Each site received a total of 25 kg of potassium bromide. The last days of July in 1990 were wet. The water table was at or near the ground surface at the Dry Lake, Williamson, and Rucks sites. Rainfall punctuated the tracer application procedure at some locations.

Figure 4-21 provides a graphical description of the tracer placement in the soil profile. Wells were spaced approximately 3 meters apart over the 66 meters of the injection row. Surface-applied tracers created a 3 meter wide blanket over the well row. The injected bromide can be viewed as a pseudo line source placed approximately 60

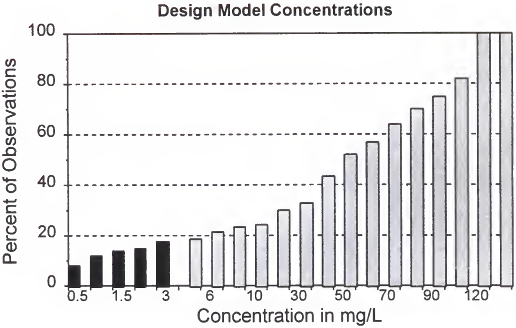

Figure 4-20. Distribution of expected bromide tracer concentration observations as plume passes the "E" row at Larson Dairy #6. Less than 20% of observations are below the design detection limit of 4 mg/L.

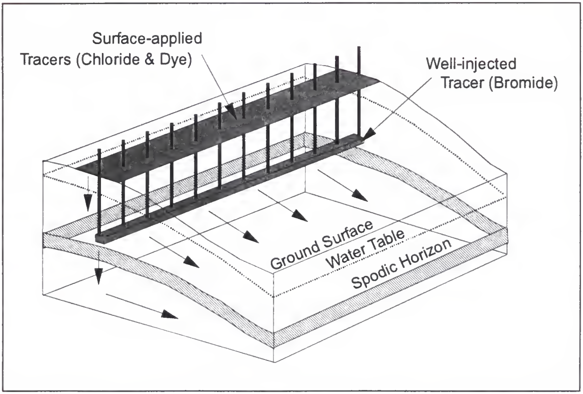

Figure 4-21. Schematic diagram of pasture soil profile and placement of tracers .

to 90 cm below the ground surface at the W. F. Rucks, Dry Lake and Williamson sites and 120 cm below the ground surface at the Larson site.

Sampling

Sampling of ground water for presence of the chloride and bromide tracers was accomplished using two methods. The shallow wells were sampled using bailer and pump methods. Wells along the application row which served as bromide injection points were not sampled in the months immediately following introduction of the tracers. However, every third well along the application row (the wells into which bromide was not injected) was included in the regular sampling schedule.

Water samples extracted from soil core samples were analyzed for bromide content. As described in the hydrologic monitoring section, these cores were obtained to a depth of 13 meters. After removal, a 500 g representative section of the core was stored in glass jars and shipped to the Gainesville laboratory for analysis. In the process of drilling to secure the core samples, large volumes of water from external sources were used to mix the bentonite mud needed to stabilize the drilled cavity. Core samples were acquired by rotary drilling to the sampling depth followed by driving a split spoon sampler into the bottom of the cavity which was subsequently lifted through the mud-filled cavity to the surface. To minimize the opportunity for contamination, the end of the split spoon sampler was sealed with tape prior to insertion. The tape seal was broken once the sampler reached the bottom of the cavity and was driven into the profile. Despite this precaution, it is possible that the samples may have been exposed to non-native water and mud.

Laboratory Analysis

Ion chromatography was used to analyze ground water samples for the presence of the bromide and chloride tracers. Water samples taken from the Larson site required pretreatment to remove nitrate interferences. Development of the sample preparation procedure and treatment is described in Appendix A. Prior to analysis, samples were filtered through a 0.45 micron filter. The filtered sample was run through a DIONEX QIC Ion Chromatograph equipped with an NG-1 humics guard column, an AG4A concentrator column, an AS4A anion separator column and a conductivity cell detector. The eluant consisted of 2 mM Na_2CO_3 and 4 mM $NaHCO_3$ solution pumped at a rate of 1.5 mL per minute. A 0.25 mM H_2SO_4 solution with a flow rate of 3 mL per minute served as the suppressor regenerant.

In addition to a large number of samples taken at regular intervals from the wells, a set of water samples extracted from the soil cores was also analyzed for presence of the bromide tracer. Once returned to the laboratory, the soil samples were checked for moisture content. Pore water was extracted from the material using a vacuum filter apparatus. In those cases where fine soil textures or low moisture content made it difficult to extract a sufficiently large water sample, extra water was added to the soil sample. The resulting slurry was mixed thoroughly prior to filtering. The concentrations measured in this extract were later adjusted to reflect the dilution factor.

To handle extremely difficult cases, a sequential dilution technique was developed and employed. In this process a soil sample of known moisture content was divided into four equal portions. A volume of water, typically around 50 ml was added to the first subsample and mixed. The sample was filtered to extract the water to the extent possible. This resulting filtrate was added to the next subsample, mixed and filtered. The procedure was repeated until all subsamples had been used and a final

filtrate extracted. A spreadsheet algorithm enabled calculation of the cascaded dilution factor to equate bromide concentrations in the final water sample to the original pore water concentration. Preliminary tests using spiked matrix solutions and washed sand samples from Larson Dairy validated the accuracy of the sequential dilution procedure and algorithm.

Salt Tracer Movement

Salt tracer (chloride and bromide) experiments were initiated in July of 1990. During the 17 months from July, 1990 to December, 1991 more than 5000 ground water samples were taken from the 550 wells located on the four pasture sites. More than 4000 of these samples were analyzed for presence of the salt tracers to determine the vertical and lateral movement of the tracers as they were carried. In addition, more than a year after application of the salt tracers, soil cores from two locations on each monitoring site were extracted and the pore water analyzed for bromide content. The points investigated in December, 1991 were the C16 and D3 locations at Dry Lake Dairy #1 and the D7 and E3 locations on W.F. Rucks Dairy. The points investigated in August, 1991 were the C12 and F1 locations at Larson Dairy #6 and the C15 and D2 locations of Williamson Ranch.

Results describing the distribution of tracers deep in the soil profile cannot be viewed with the same high degree of confidence as can be assigned to the lateral movement results, since lateral movement results are based on hundreds of well samples while vertical distribution results are based on only two soil cores extracted at each site.

Tracer detection in the area directly beneath the application row was limited by factors of well placement and the choice of wells to be sampled. These factors should

be considered in interpreting results. While chloride was applied uniformly over all wells of the injection row, bromide was introduced to the ground water via shallow wells. Bromide was not introduced into each third shallow well along the injection row. This shallow well along with its associated medium-depth well were used for ground water sampling. Thus, bromide tracer appearing in these medium-depth wells not only had to progress vertically from the shallow injection wells to the sampling depth but also had to traverse approximately 1.5 to 3 meters laterally from the injection point to the monitoring well. The surface-applied chloride, however, simply moved vertically to reach the monitoring wells. Another factor affecting detection of bromide tracer along the injection row was the staggering of the shallow and medium-depth wells. The center row of wells in the tracer application compound actually consisted of two rows, a row of shallow wells and a row of medium-depth wells. These rows were separated by approximately 150 cm. At two sites (Larson and Dry Lake) the medium-depth wells were 150 cm down-gradient from the shallow wells. At the other sites (Williamson and Rucks) the shallow wells were down-gradient of the medium-depth wells. Thus, at these sites the likelihood of detecting bromide in the medium-depth wells was diminished.

Larson Dairy #6. As expected, the hilly Larson site showed the highest rate of tracer movement. Within 30 days of application, the surface-applied chloride had reached the groundwater table at the C row and was appearing in both the shallow (2 meters) and medium-depth (4 meters) wells as shown in Figure 4-22 and Figure 4-23. Like chloride, bromide was also apparent in the C wells soon after tracer application, as shown in Figure 4-24 and Figure 4-25. The latter of these two figures shows how the bromide concentration in many of the medium-depth wells did not exhibit a distinct peak and recession. In some wells the concentration was slow to increase and even slower

in its decrease. Similar patterns are evident in the D and E wells as shown in Figure 4-26 and Figure 4-27.

Figure 4-28 presents a summary description of the lateral progression of the tracer plume. The plume appears to have arrived at the D row (7.5 meters from the application point) approximately 80 days after injection. Tracer appearance at the E row (7.5 meters from D row) followed approximately 100 days later. The plume was apparent at the F well station (15 meters from the E row) after an additional 140 days. It required only 40 additional days to reach the G row of wells (15 meters from the F station). After accounting for the plume vector of 45 degrees from the primary streamline, average plume speed was 0.5 cm/hr.

At the end of the data collection project (November-December, 1991) bromide concentration at all sampling points (D, E, F, and G rows) dramatically increased to approximately 20 mg/L level. This may have been caused by the relatively high water table conditions, which prevailed from September to November of that year at the Larson site. The origin of this tracer may have been secondary transport from the original injection location, but a more likely source is the soil profile above the well. Disposal of water evacuated from the well during each sampling event caused deposition of bromide in the surface horizons. Subsequent rainfall would wash this bromide back down into the water table in the immediate vicinity of the well. The slow recession and the wet season increase of the concentration curve are likely the result of this recirculation of tracer.

A year after application, soil cores showed the bromide concentrations at the application point to be highest between 4 to 8 meters below the surface with maximum concentration occurring at 5 meters. In comparing the C12 to F1 locations (see Figures 4-29 and 4-30), the bromide plume does not appear to have moved deeper in the

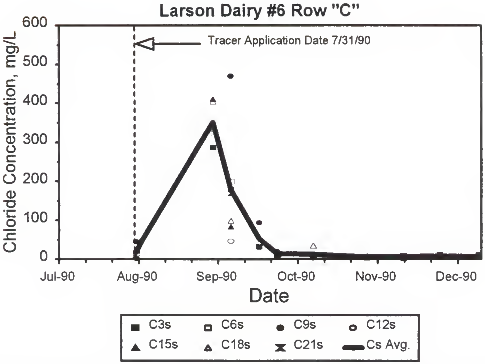

Figure 4-22. Results of chloride tracer monitoring in the shallow wells of Row "C" at Larson Dairy #6.

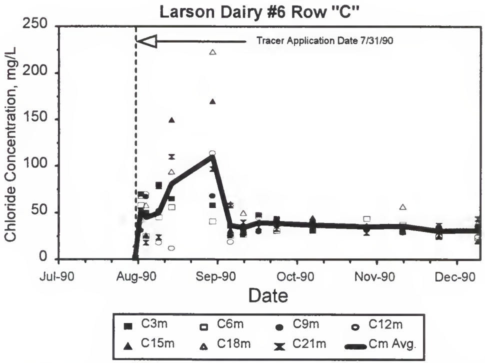

Figure 4-23. Results of chloride tracer monitoring in the medium-depth wells of Row "C" at Larson Dairy #6.

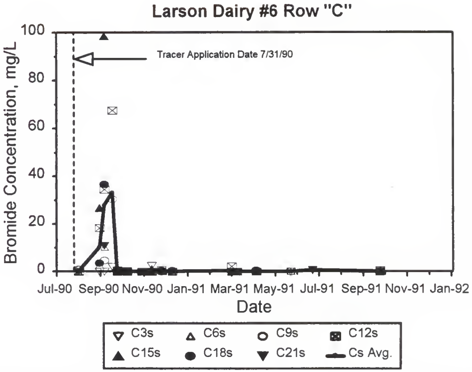

Figure 4-24. Results of bromide tracer monitoring in the shallow wells of Row "C" at Larson Dairy #6.

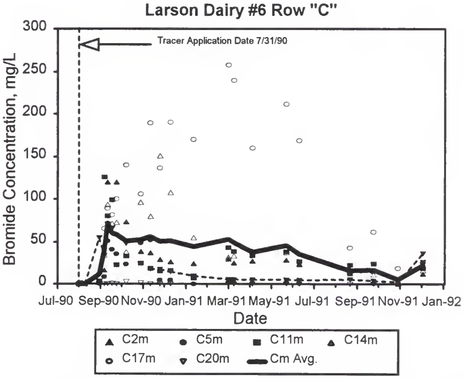

Figure 4-25. Results of bromide tracer monitoring in the medium-depth wells of Row "C" at Larson Dairy #6.

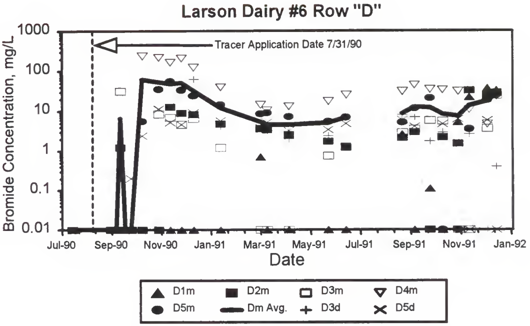

Figure 4-26. Results of bromide tracer monitoring in the medium-depth and deep wells of Row "D" at Larson Dairy #6.

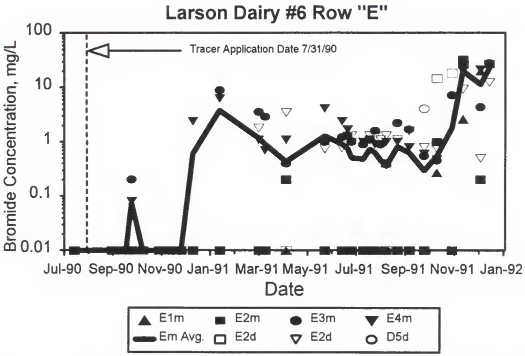

Figure 4-27. Results of bromide tracer monitoring in the medium-depth and deep wells of Row "E" of Larson Dairy #6.

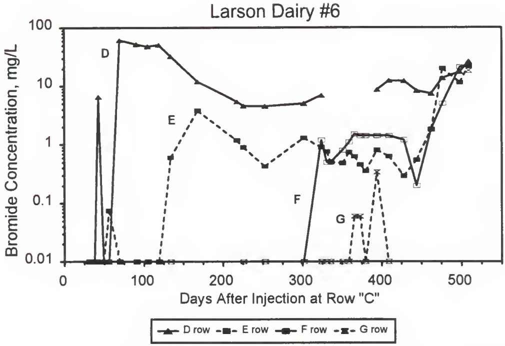

Figure 4-28. Results of bromide tracer monitoring in the wells of Larson Dairy #6.

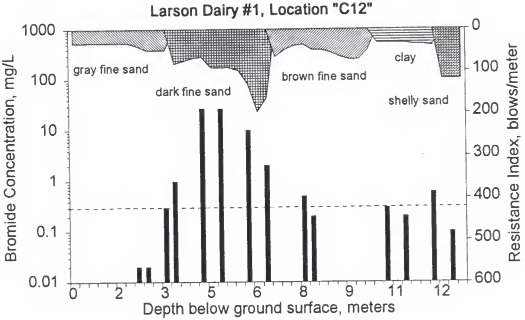

Figure 4-29. Measurements of bromide concentrations in the deep soil profile of location C12 at Larson Dairy #6.

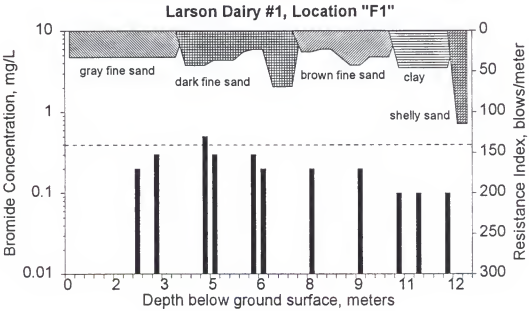

Figure 4-30. Measurements of bromide concentrations in the deep soil profile of location F1 at Larson Dairy #6.

profile; maximum tracer concentration remained at 5 meters. At location F1 almost all bromide detections were below the threshold of doubt concentration set at 0.3 mg/L, the concentration of bromide in the water used during the drilling process for extracting the cores. Values below this threshold may reflect contamination by drilling water rather than presence of the ground water tracer.

W.F. Rucks Dairy. Subsurface lateral movement of bromide at the Rucks pasture was the slowest of the four sites. The chloride tracer appeared in the shallow injection row wells within 15 days of application (Figure 4-31) and in the medium-depth wells 60 days after application (Figure 4-32). Discerning the arrival of bromide in the injection row wells is not possible from the data results as shown in Figure 4-33 and Figure 4-34. However, the bromide plume arrived at the E row wells (7.5 meters from the injection point) 400 days after application (see Figure 4-35 and Figure 4-36). While Figure 4-35 shows the appearance of bromide in the shallow wells only two months after application, this tracer is likely not the result of subsurface transport but rather the result of surface transport. Soon after application, bromide was redeposited on the ground surface as a result of well water purges from the D row wells as part of the sampling protocol. The actual subsurface bromide plume an the E row wells was most apparent in one of the deep wells (6 meter) rather than in any of the medium-depth wells (3 meters). After accounting for the plume vector of 24 degrees from the primary streamline, average plume speed was 0.08 cm/hr.

The W.F. Rucks Dairy soil core data shown in Figure 4-37 and Figure 4-38 document the bromide tracer to be present at the D7 location between 1 and 3 meters below the ground surface. Similar concentrations were measured for the E3 location. However, additional elevated bromide concentrations were observed between 6 and 12 meters at the D7 location. This bimodal distribution may be caused by recirculation of

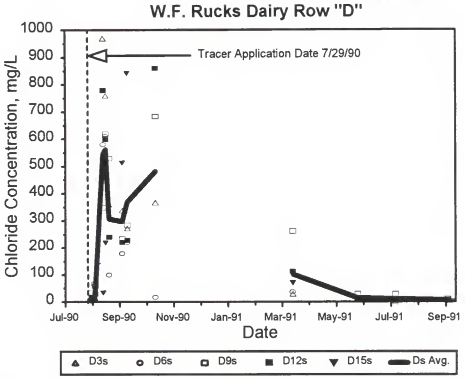

Figure 4-31. Results of chloride tracer monitoring in the shallow-depth wells of Row "D" at W.F. Rucks Dairy.

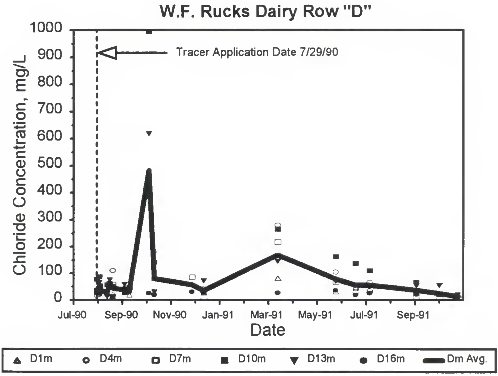

Figure 4-32. Results of chloride tracer monitoring in the medium-depth wells of Row "D" at W.F. Rucks Dairy.

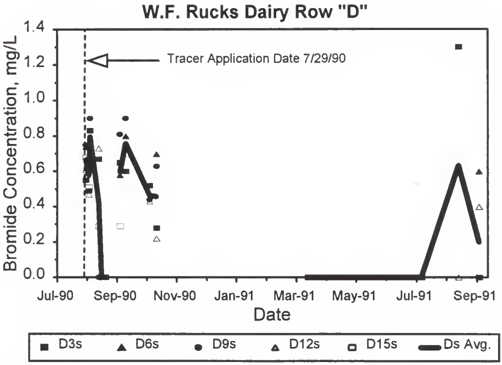

Figure 4-33. Results of bromide tracer monitoring in the shallow wells of Row "D" at W.F. Rucks Dairy.

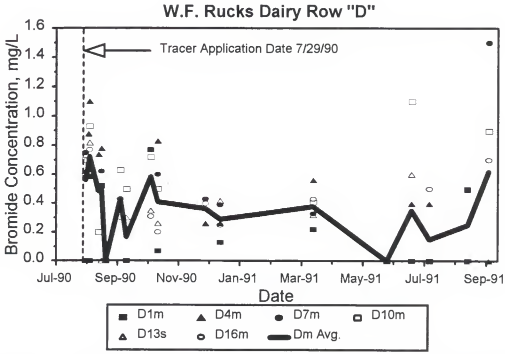

Figure 4-34. Results of bromide tracer monitoring in the medium-depth wells of Row "D" at W.F. Rucks Dairy.

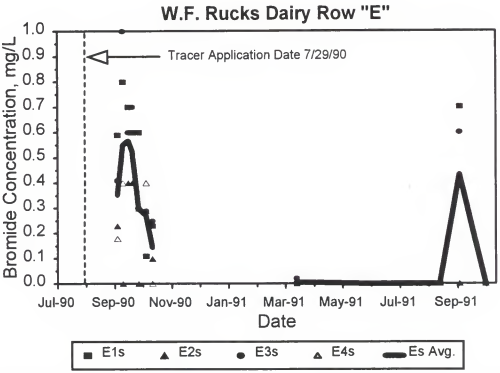

Figure 4-35. Results of bromide tracer monitoring in the shallow wells of Row "E" of W.F. Rucks Dairy.

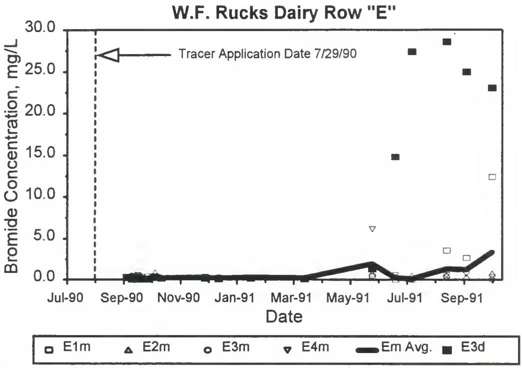

Figure 4-36. Results of bromide tracer monitoring in the medium-depth and deep wells of Row "E" at W.F. Rucks Dairy.

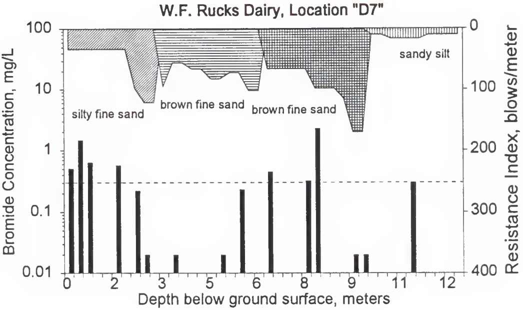

Figure 4-37. Measurements of bromide concentrations in the deep soil profile of location D7 at W.F. Rucks Dairy.

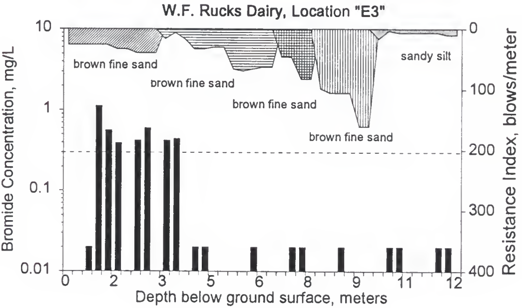

Figure 4-38. Measurements of bromide concentrations in the deep soil profile of location E3 at W.F. Rucks Dairy.

bromide extracted from the deeper well which is deposited on the ground surface in the process of sampling. Thus, at the D7 location the deeper occurrence of bromide is more likely to represent tracers transported by subsurface flow from the point of tracer application. The same cannot be said for the E3 location. The assertion that the bromide in the profile above 4 meters was derived from recirculation was not supported by detection of bromide in core samples deeper than 4 meters below ground surface. However the well data for the same E3 location clearly documented bromide at these depths. These data suggested that slow lateral movement provided opportunity for significant downward movement of ground water to occur at the Rucks site. It also suggested that a single core sample was not sufficient to draw conclusions regarding bromide distribution in the soil profile.

Williamson Ranch. The Williamson site showed the second highest lateral advective transport rate. Figure 4-39 describes the concentration of chloride observed in the shallow wells of the injection row and Figure 4-40 provides the same information for the medium-depth wells. Concentration in the medium-depth wells peaked approximately 15 days after application. The shallow wells showed earlier appearance but also exhibited evidence of tracer recirculation. Williamson was the only site at which the chloride plume was observed beyond the application row. Figure 4-41 and Figure 4-42 document chloride at the D row. Figure 4-43 and Figure 4-44 are for chloride at the E row wells. Plume arrival in the D row was first observed in December of 1990 with highest concentration observed in March of 1991. Similarly, bromide (see Figure 4-45) reached the D row in December and peaked in March. Some wells in the D row showed a much later arrival of both chloride and bromide. Along the E row, chloride and bromide (Figure 4-46) appeared in the medium-depth wells in August/September of 1991 and peaked between September and November.

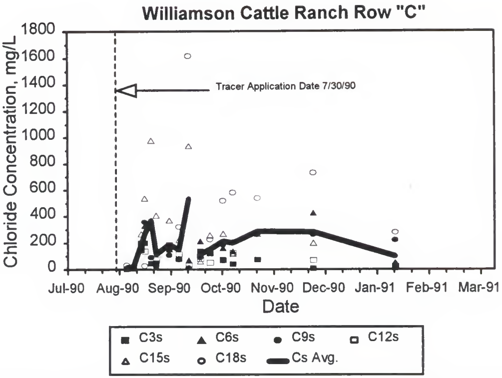

Figure 4-39. Results of chloride tracer monitoring in the shallow wells of Row "C" at Williamson Cattle Ranch.

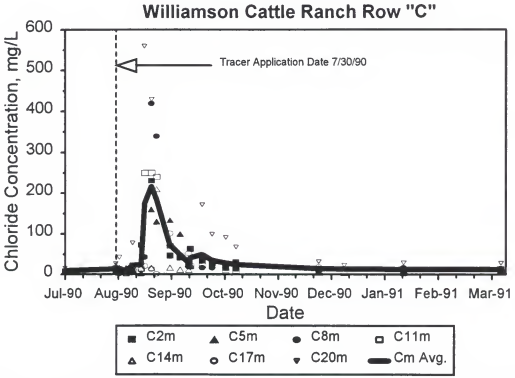

Figure 4-40. Results of chloride tracer monitoring in the medium-depth wells of Row "C" at Williamson Cattle Ranch.

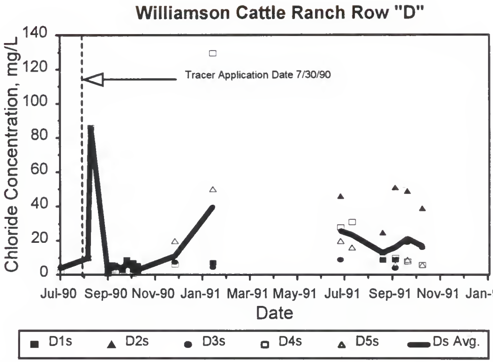

Figure 4-41. Results of chloride tracer monitoring in the shallow wells of Row "D" at Williamson Cattle Ranch.

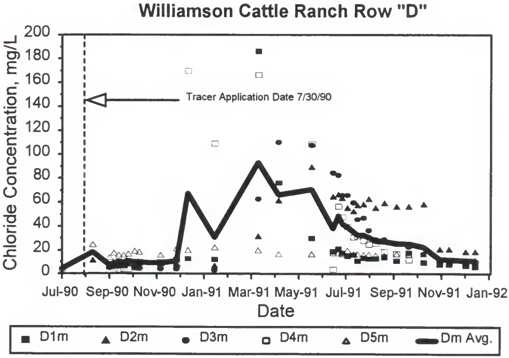

Figure 4-42. Results of chloride tracer monitoring in the medium-depth wells of Row "D" at Williamson Cattle Ranch.

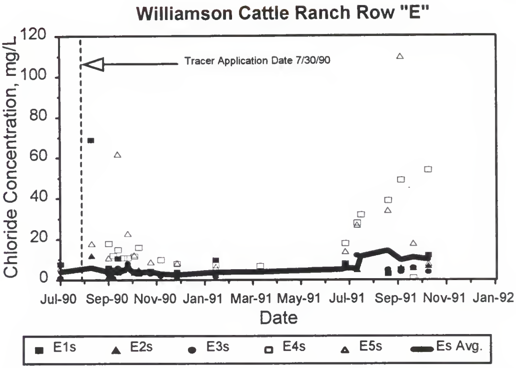

Figure 4-43. Results of chloride tracer monitoring in the shallow wells of Row "E" at Williamson Cattle Ranch.

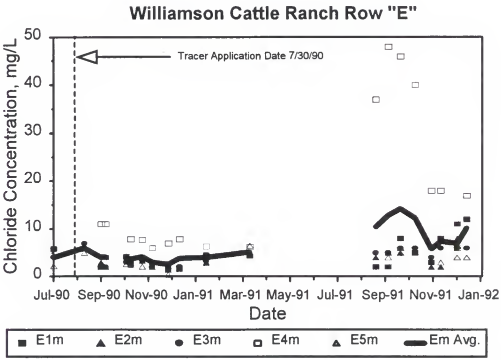

Figure 4-44. Results of chloride tracer monitoring in the medium-depth wells of Row "E" at Williamson Cattle Ranch.

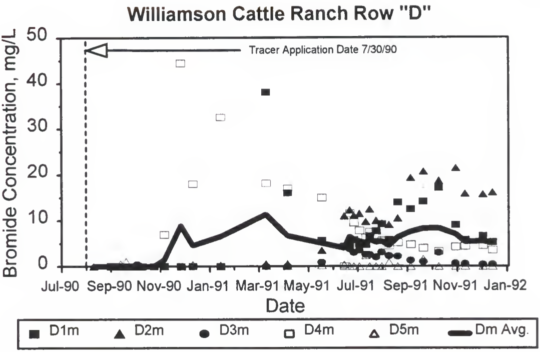

Figure 4-45. Results of bromide tracer monitoring in the medium-depth wells of Row "D" at Williamson Cattle Ranch.

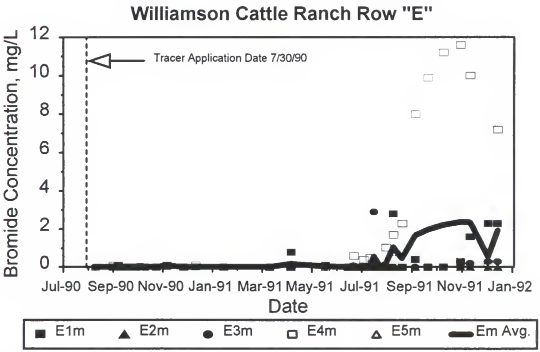

Figure 4-46. Results of bromide tracer monitoring in the medium-depth wells of Row "E" at Williamson Cattle Ranch.

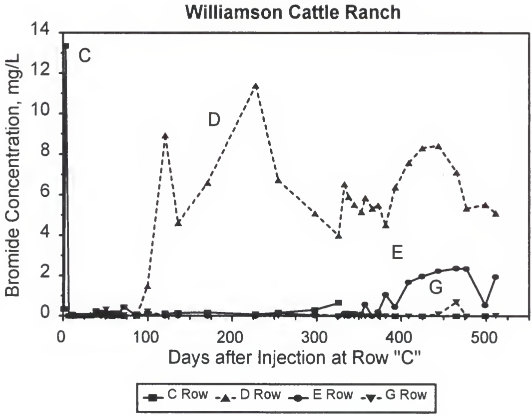

Figure 4-47. Results of bromide tracer monitoring in the wells of Williamson Cattle Ranch.

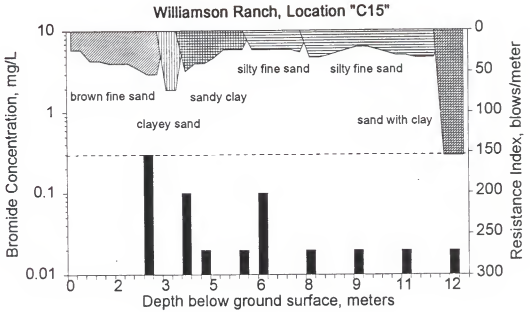

Figure 4-48. Measurements of bromide concentrations in the deep soil profile of location C15 at Williamson Cattle Ranch.

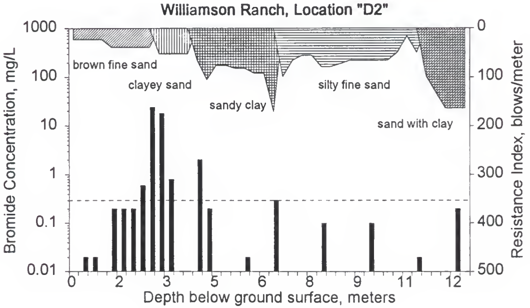

Figure 4-49. Measurements of bromide concentrations in the deep soil profile of location D2 at Williamson Cattle Ranch.

Figure 4-47 presents a summary of bromide movement with the ground water of Williamson Ranch. Some evidence of plume arrival at the G row was observed, however these observations were few and weak. Taking into account observations at the D and E rows, the plume moved at an average rate of 0.16 cm/hr across the Williamson site during the study period.

Core sample determination of vertical tracer distribution at Williamson Ranch showed the bromide concentration is highest between 1.5 and 3 meters below ground surface (see Figure 4-48 and 4-49). This relatively shallow occurrence may have been the result of the clay horizon which began at 3 to 4 meters. In moving from the C15 to D2 location, the tracer did not appear to have moved deeper into the profile. Very little bromide tracer was found remaining in the profile at the application point (C row) suggesting a high degree of flushing of the upper soil profile.

Dry Lake Dairy #1. Due to a high density of livestock, background concentrations of chloride were extremely high at the Dry Lake site. This factor, combined with the low water table gradient yielded inconclusive chloride tracer results. Figure 4-50 and Figure 4-51 demonstrate the difficulty in defining appearance of the chloride tracer in both the shallow and medium-depth wells. Movement of the bromide tracer from the shallow injection wells to the deeper monitoring wells was slow, requiring over 2 months travel time (see Figure 4-52 and Figure 4-53). Lateral movement of the plume to the D row wells (7.5 meters from the application point) was also difficult to pin-point(see Figure 4-54 and Figure 4-55). The same held true for the E row wells (Figure 4-56 and Figure 4-57). While an exact calculation was difficult with such slow movement and few positive tracer appearances, approximate plume velocity is 0.09 cm/hr, determined using a July, 1991 arrival at the D row and an October, 1991 arrival at the E row.

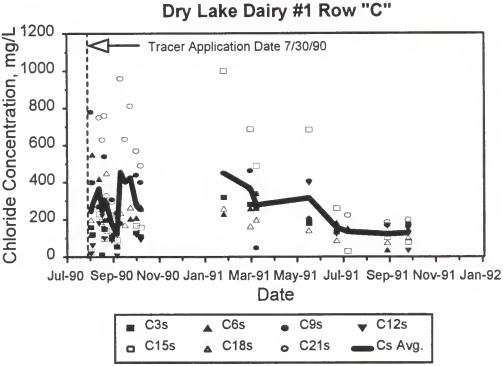

Figure 4-50. Results of chloride tracer monitoring in the shallow wells of Row "C" at Dry Lake Dairy #1.

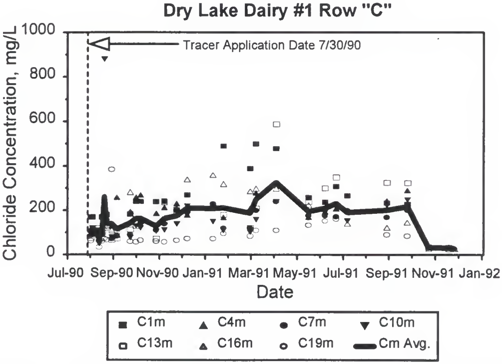

Figure 4-51. Results of chloride tracer monitoring in the medium-depth wells of Row "C" at Dry Lake Dairy #1.

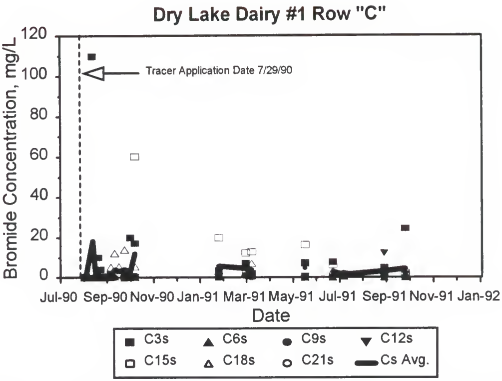

Figure 4-52. Results of bromide tracer monitoring in the shallow wells of Row "C" at Dry Lake Dairy #1.

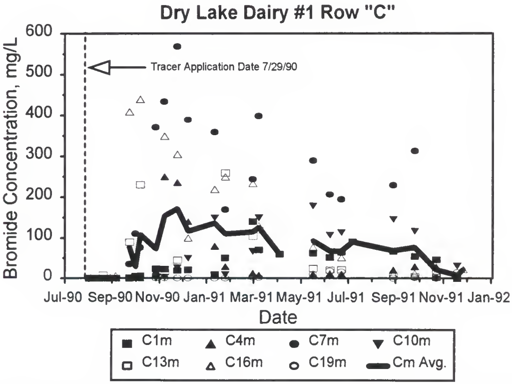

Figure 4-53. Results of bromide tracer monitoring in the medium-depth wells of Row "C" at Dry Lake Dairy #1.

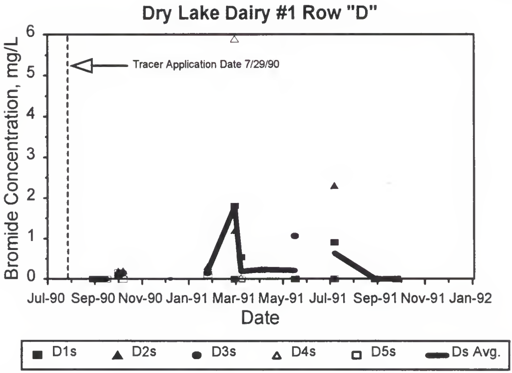

Figure 4-54. Results of bromide tracer monitoring in the shallow wells of Row "D" at Dry Lake Dairy #1.

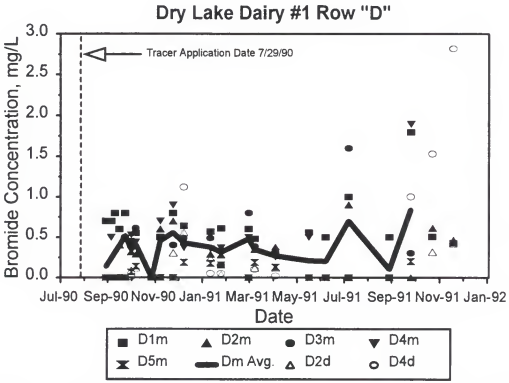

Figure 4-55. Results of chloride tracer monitoring in the medium-depth wells of Row "D" at Dry Lake Dairy #1.

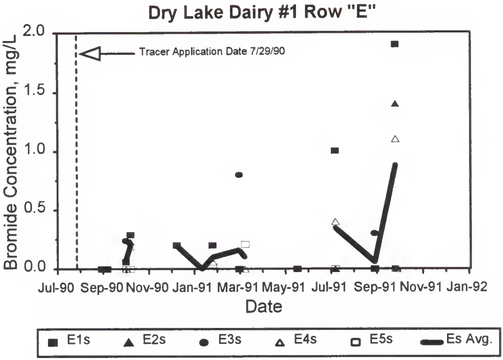

Figure 4-56. Results of bromide tracer monitoring in the shallow wells of Row "E" at Dry Lake Dairy #1.

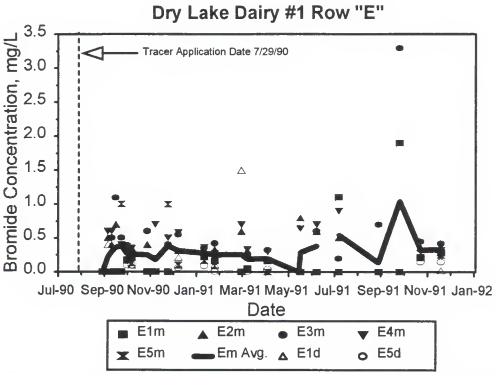

Figure 4-57. Results of bromide tracer monitoring in the medium-depth wells of Row "E" at Dry Lake Dairy #1.

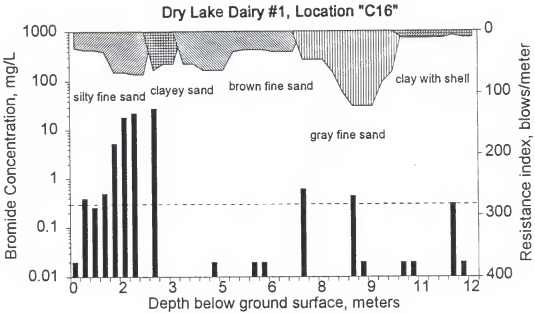

Figure 4-58. Measurements of bromide concentrations in the deep soil profile of location C16 at Dry Lake Dairy #1.

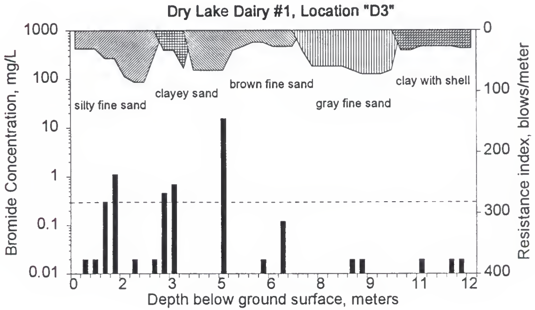

Figure 4-59. Measurements of bromide concentrations in the deep soil profile of location D3 at Dry Lake Dairy #1.

The Dry Lake Dairy #1 D3 soil core data presented in Figure 4-58 show the tracer to be present between the depths of 1 and 5 meters with the highest concentration measured at 5 meters below the ground surface. For the C16 location on the same site (Figure 4-59), the tracer appeared to be concentrated between 1.5 and 3 meters below the ground surface. Elevated bromide concentrations (0.3-0.8 mg/L) were recorded below 6 meters, but these data were inconsistent. As pointed out previously, the water used as the drilling mud for the coring process was measured to contain 0.3 mg/L bromide. Pore water measurements in this range may be the result of drilling mud contamination or pasture background rather than a true reflection of tracer movement. Nevertheless the data suggested that as the tracer plume progresses from the C row to the D row, the plume moved deeper into the profile, starting from about 2.5 meters and moving to about 5 meters below the ground surface.

Model Comparison

Rainfall conditions following the chloride tracer application on the last few days of July, 1990 were much more favorable. Each site received between 13 and 18 cm of rain within a two-week period following initiation date. Like the Rhodamine WT test, two of the four sites, Williamson and Rucks, showed tracer peaks in the shallow ground water wells. The tracer was apparent in these wells between 15 and 16 days following application. The Dry Lake site did not generate a distinct chloride peak due to the unusually high background chloride concentrations in the shallow ground water. Larson was also a difficult site during the early chloride tracer test. Its shallow wells went dry until the end of August at which time the tracer had long since reached the medium-depth (4 meter) wells. The results at Williamson and Rucks provided a reasonable match with the CHEMFLO simulation results described in the dye tracer

section. Both the field and model results suggested that the contaminant would reach the shallow well horizon after approximately 13 cm of rainfall.

Results of data collection demonstrated several limitations to the applicability of the advective-dispersive analytical model. The linear superposition design scenario assumed a flow direction orthogonal to the injection and monitoring well rows. However, each site showed some ground water streamline deviation form the direction of the primary transect. One implication was that the orientation of the plumes is such that the analytical model's concentration profile axis flow vector was not parallel with the monitoring well row (see Figure 4-60). The model was adjusted to account for the longitudinal offset caused by the lack of coincidental axes. Another implication was the effective separation distance between adjacent plume streamlines which were drawn nearer to one another by the flow angle. This too was adjusted in the linear superposition algorithm. Similarly, the travel distance experienced by the plume in reaching the monitoring well row was increased by the angle of the flowpath and was addressed in the analytical model.

Results of tracer monitoring were compared with the original design model applied to the Williamson and Larson sites. In generating this comparison, several factors were adjusted. Among these were the vertical distribution of the tracer plume as suggested by the deep soil boring and deep well measurements. Another adjusted parameter was the plume mass and dispersivity.

Figure 4-61 shows a simulated plume with center of mass located 3 meters from its injection well origin. At this point the distance from the plume center to the monitoring well along the "C" row is approximately 2 meters. Tracer concentration measurements from the "C" row monitoring wells showed bromide concentrations far in

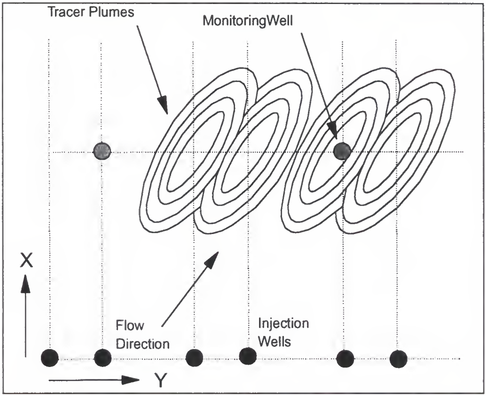

Figure 4-60. Deviation of ground water flow streamline from direction of primary well transect.

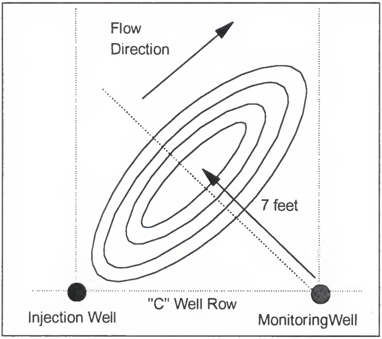

Figure 4-61. Orientation of tracer plume relative to Larson "C" row monitoring well.

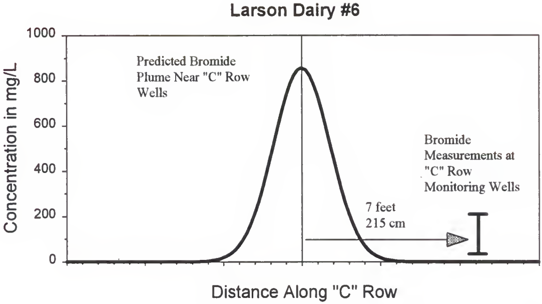

Figure 4-62. Comparison of simulated tracer plume to actual tracer measurements at the "C" row monitoring wells of Larson Dairy #6.

excess of what could be explained by dispersion (see Figure 4-62), regardless of whatever reasonable coefficient of transverse dispersivity was employed.

This high observed concentration could be attributed to the physical modification of flow patterns induced through the act of sampling the monitoring wells. The frequency and volume of purge and sample water extracted from the well introduced an intermittent lateral flow component, thus spreading the plume more than would be caused by the natural dispersion of the groundwater tracer.

The analytical model was calibrated to the field observations using the adjustment parameters cited above. Model calibration results for the "D" and "E" rows of Larson Dairy are shown in Figures 4-63 through 4-65 and in Tables 4-6 through 4-8. At the Larson site, reasonable results were achieved by reducing the tracer mass within the idealized plume. In addition, the coefficient of dispersion was reduced from the design value of 10 to 5 and the ratio of longitudinal to transverse dispersivity was changed to 10:3. This relatively low ratio was reasonable given the sampling-induced transverse flow near the injection and monitoring rows.

The tracer mass reduction was warranted by the impact of the monitoring well sampling. Long term measurements showed that the extraction and surface redeposition of tracers fixed large quantities of the tracers in the local vicinity of these wells. From the "C" row to the "D" row, 16% of the tracer was assumed to have been effectively lost to the idealized plume system. Between the "D" and "E" rows an equal quantity was assumed detained/lost.

The model results generated for the "D" row appear plausible. The median peak bromide concentration measured along the "D" row was 50 mg/L. The model average was 80 mg/L. The range (high and low) of the measured values also

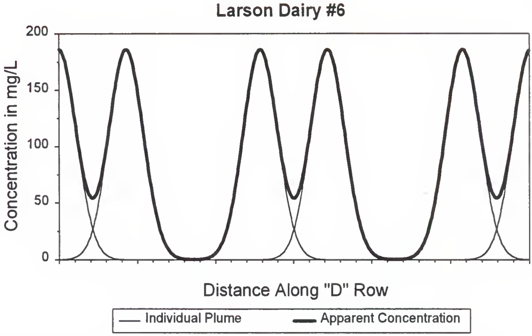

Figure 4-63 Calibrated model results for tracer plume concentration profile along the "D" row of Larson Dairy #6.

Table 4-6. Comparison of field measurements of tracer plume characteristics to design and calibrated model results for the "D" row of Larson Dairy #6.

Parameter	Measured	Calibrated Model	Design Parameter
Plume Velocity	0.42 cm/hr (0.33 ft/day)	0.42 cm/hr (0.33 ft/day)	1 cm/hr (0.79 ft/day)
Travel Distance	1000 cm (35 ft)	1000 cm (35 ft)	760 cm (25 ft)
Spacing Between Center of Plumes	215 cm (7 ft)	215 cm (7 ft)	300 cm (10 ft)
Highest Peak Concentrations	250 mg/L	190 mg/L	220 mg/L
Lowest Peak Concentration	20 mg/L	0 mg/L	0 mg/L
Percent above Detection Limit	100%	87%	74%
Median Peak Concentration	50 mg/L	80 mg/L	40 mg/L
Tracer Mass in Plume		1600 g	1900 g
Vertical Distribution Length		250 cm	200 cm
Longitudinal Dispersivity		5 cm	10 cm
Transverse Dispersivity		1.5 cm	2 cm

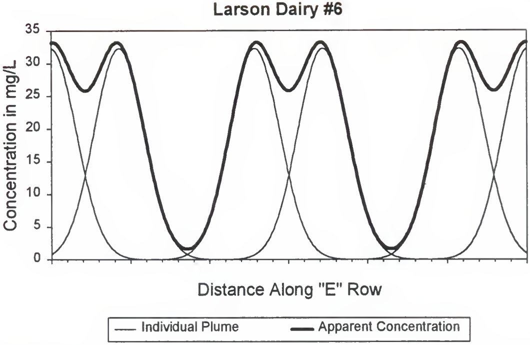

Figure 4-64. Calibrated model results for tracer plume concentration profile along the "E" row of Larson Dairy #6.

Table 4-7. Comparison of field measurements of tracer plume characteristics to design and calibrated model results for the "E" row of Larson Dairy #6.

Parameter	Measured	Calibrated Model	Design Parameter
Plume Velocity	0.42 cm/hr (0.33 ft/day)	0.42 cm/hr (0.33 ft/day)	1 cm/hr (0.79 ft/day)
Travel Distance	2100 cm (70 ft)	2100 cm (70 ft)	1500 cm (50 ft)
Spacing Between Center of Plumes	215 cm (7 ft)	215 cm (7 ft)	300 cm (10 ft)
Highest Peak Concentrations	6 mg/L	33 mg/L	110 mg/L
Lowest Peak Concentration	0.2 mg/L	0 mg/L	0 mg/L
Percent above Detection Limit	50%	89%	82%
Median Peak Concentration	4 mg/L	26 mg/L	50 mg/L
Tracer Mass in Plume		1400 g	1900 g
Vertical Distribution Length		600 cm	200 cm
Longitudinal Dispersivity		5 cm	10 cm
Transverse Dispersivity		1.5 cm	2 cm

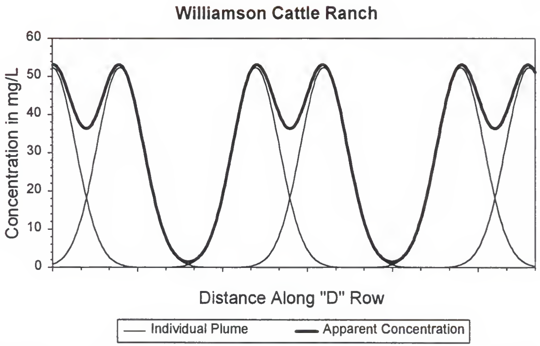

Figure 4-65. Calibrated model results for tracer plume concentration profile along the "D" row of Williamson Cattle Ranch.

Table 4-8. Comparison of field measurements of tracer plume characteristics to design and calibrated model results for the "D" row of Williamson Cattle Ranch.

Parameter	Measured	Calibrated Model	Design Parameter
Plume Velocity	0.14 cm/hr (0.11 ft/day)	0.14 cm/hr (0.11 ft/day)	1 cm/hr (0.79 ft/day)
Travel Distance	850 cm (28 ft)	850 cm (28 ft)	760 cm (25 ft)
Spacing Between Center of Plumes	240 cm (7.9 ft)	240 cm (7.9 ft)	300 cm (10 ft)
Highest Peak Concentrations	45 mg/L	53 mg/L	220 mg/L
Lowest Peak Concentration	0 mg/L	2 mg/L	0 mg/L
Percent above Detection Limit	60%	88%	74%
Median Peak Concentration	5 mg/L	40 mg/L	40 mg/L
Tracer Mass in Plume		1600 g	1900 g
Vertical Distribution Length		250 cm	200 cm
Longitudinal Dispersivity		10 cm	10 cm
Transverse Dispersivity		2 cm	2 cm

appeared reasonable when compared to an inspection of the variability within the simulated concentration profile (see Table 4-6).

The comparison was not as favorable at the "E" row (see Table 4-7). Model results suggested that higher concentrations should have been observed in the monitoring wells. Efforts to calibrate the model results to match the lower field measurements were attempted within reason, but this did not completely eliminate the overestimation. In addition to reducing the mass as described above, the plume mass was assumed to be distributed over a much larger vertical range (6 meters) than was assumed at the "D" rows (2 meters).

Model calibration results for the Williamson site are shown in Table 4-8 and Figure 4-65. The design values of the dispersivity were double for the calibration model. This seemed reasonable given the hard spodic horizon on top of which the tracer solution was deposited. Passage of the tracers through and on top of this layer would be expected to distribute the bromide over a larger region of the soil profile. Reasonable results were achieved from the calibrated model. The highest measured peak (45 mg/L) was near the calibrated model peak (53 mg/L).

CHAPTER 5
GROUND WATER QUALITY INVESTIGATIONS

The four pasture sites were studied to determine how the concentration of phosphorus in the surface and ground water may be related to hydrologic, topographic, and land use characteristics of the sites. A further goal was to estimate off-site phosphorus loading by the pasture sites which is carried by subsurface flow.

The hydrologic investigations section of this study (Chapter 3) documents the significant differences in water budget components, topographic features and other hydrologic characteristics. The tracer investigations (Chapter 4) section documents the differences in ground water movement characteristics for the pasture study sites. A third critical piece of information in relating these factors to a site's potential for contaminant transport is information documenting the ground water quality characteristics of the sites.

In addition, these investigations into ground water quality led to reconsideration of the methods by which sampling was accomplished on the sites. This issue of sampling protocol has significance not only to the issue of water quality investigations, but also to the question of appropriate sampling methods for tracer investigations. Sampling protocol is addressed as a separate issue in Appendix B. While the sampling protocol section establishes that monitoring wells can produce reasonable estimates of ground water quality in the immediate vicinity of the sampling location, it did not establish that a limited number of sampling points can accurately describe the water quality of an entire site. This fact should qualify the interpretations of the results of the

ground water phosphorus concentration data presented in this section. Despite this limitation, it is expected that limited ground water quality data useful in determining whether the various hydrologic, topographic, and land use attributes of the sites translate into measurable differences in water quality and thus, contaminant transport potential.

Sampling Procedures

Well stations designated for groundwater quality monitoring were established at each of the four research pastures. These were locations F1 and N1 at Larson Dairy #6, G1 and M1 at W.F. Rucks Dairy, WQ1 (near G2) and WQ2 (near J5) at Williamson Cattle Ranch, and G5 and K2 at Dry Lake Dairy #1. Due to problems with inquisitive cows, well locations outside the tracer application compound at the Dry Lake site were protected by small fence enclosures. Well locations within the tracer application compound were isolated by fencing at all sites, but Dry Lake conditions required additional protection. The water quality well locations at this site, G5 and K2, were not protected by fencing, but rather by concrete reinforcement. Fencing was not considered appropriate as it introduced the potential of modifying shallow water quality conditions by excluding animal traffic and waste from the ground surface in the vicinity of the monitoring well.

Samples were extracted from the wells using bailers or manual diaphragm pumps. Wells were evacuated of three casing volumes prior to sample extraction. Samples were immediately refrigerated and transported to the Okeechobee laboratory where they were filtered and transported to Gainesville. Nutrient analysis of the samples was completed by the Soil and Water Science Department laboratories.

Reported constituents included total phosphorus, soluble reactive phosphorus, ammonia, nitrate and total nitrogen.

Phosphorus Concentration Results

Total phosphorus data from wells at each of the four sites are presented in Figures 5-1 through 5-9. The data reflect improvement, or at least lack of degradation, of water quality with increasing depth at all sites. Average total phosphorus concentration measured in each observation well over the period of record is shown in Table 5-1. The concentration differences among the sites reflect differences in land use intensity. Wells on the low livestock density sites (Williamson and Rucks) exhibit low total phosphorus concentrations, less than 1 mg/L. The intensely grazed sites (Dry Lake and Larson) show much greater phosphorus concentrations. Both the Dry Lake data (Figure 5-9) and Larson data (Figure 5-1) show very high concentrations (10-50 mgP/l) of total phosphorus in the more shallow ground water. As water moves into the deeper horizons higher in organic content, phosphorus concentration drops dramatically at Dry Lake becoming less than 0.25 mg/L in the 3-meter and 6-meter wells. At Larson, however, little improvement in water quality occurs below the spodic horizon on the upslope portion of the pasture; both readings are above 25 mg/L on average. As mentioned above, the soils on this site consist of very deep, coarse sands with a barely detectable spodic horizon. A significant improvement does occur in the downslope area where the spodic becomes well defined and total phosphorus concentrations decrease to less than 2.5 mgP/L. These data combined with the water table observations depicted in Figure 3-19 suggest that in the upslope area, ground water of poor quality is ponded and isolated from the ground water of higher quality near the creek.

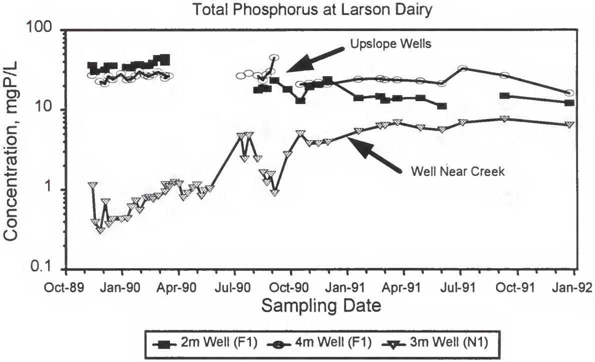

Figure 5-1. Total phosphorus concentration measured in ground water samples from monitoring wells at Larson Dairy #6.

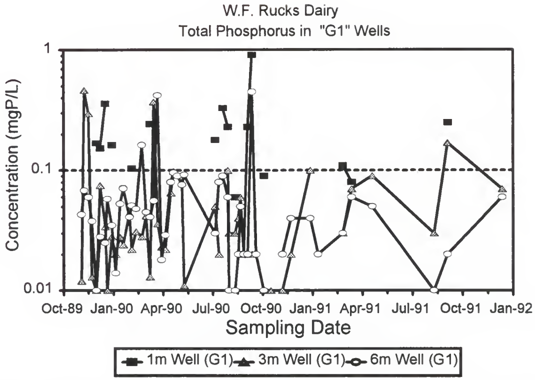

Figure 5-2. Total phosphorus concentration measured in ground water samples from monitoring wells at location G1 of W.F. Rucks Dairy.

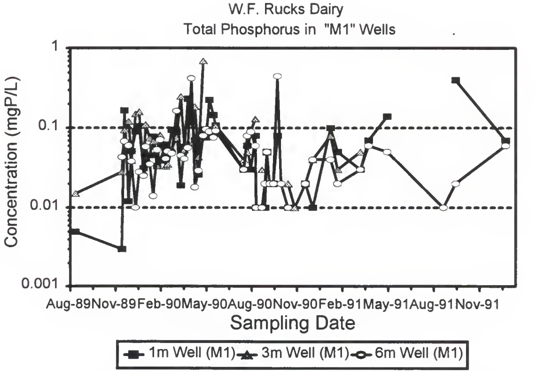

Figure 5-3. Total phosphorus concentration measured in ground water samples from monitoring wells at location M1 of W.F. Rucks Dairy.

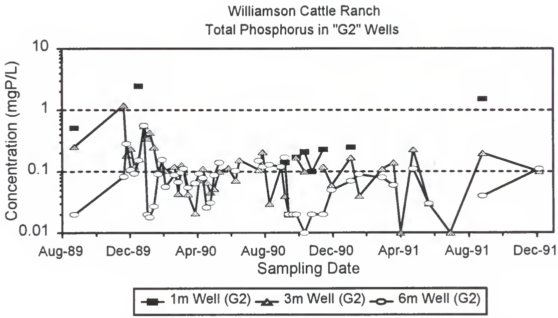

Figure 5-4. Total phosphorus concentration measured in ground water samples from monitoring wells at location G2 of Williamson Cattle Ranch.

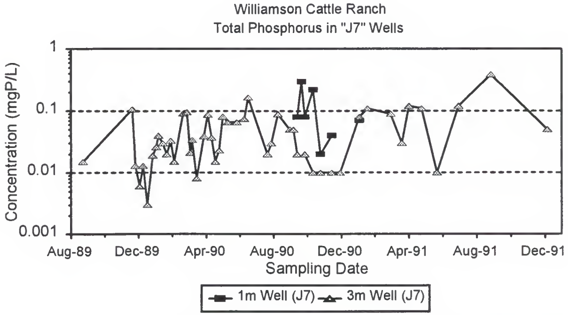

Figure 5-5. Total phosphorus concentration measured in ground water samples from monitoring wells at location J7 of Williamson Cattle Ranch.

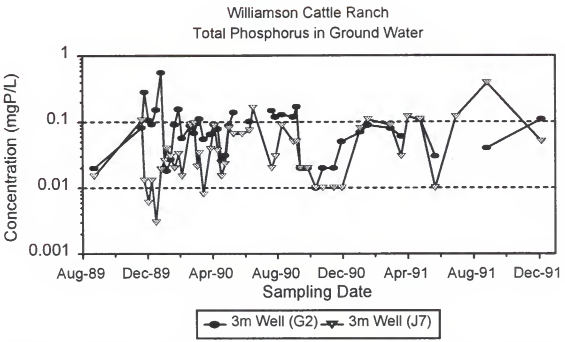

Figure 5-6. Total phosphorus concentration measured in ground water samples from medium-depth monitoring wells at locations G2 and J7 of Williamson Cattle Ranch.

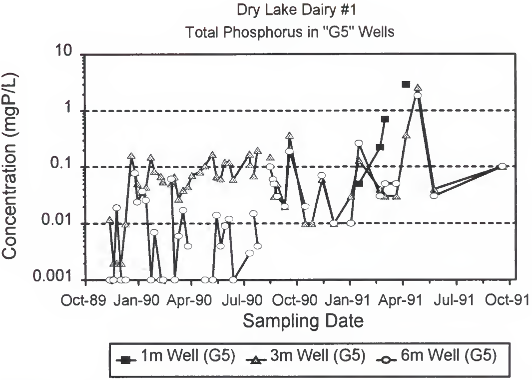

Figure 5-7. Total phosphorus concentration measured in ground water samples from monitoring wells at location G5 of Dry Lake Dairy #1.

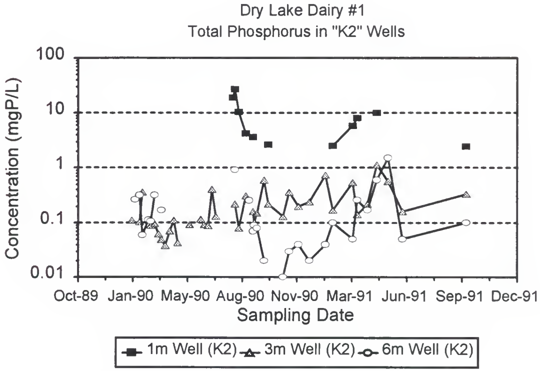

Figure 5-8. Total phosphorus concentration measured in ground water samples from monitoring wells at location K2 of Dry Lake Dairy #1.

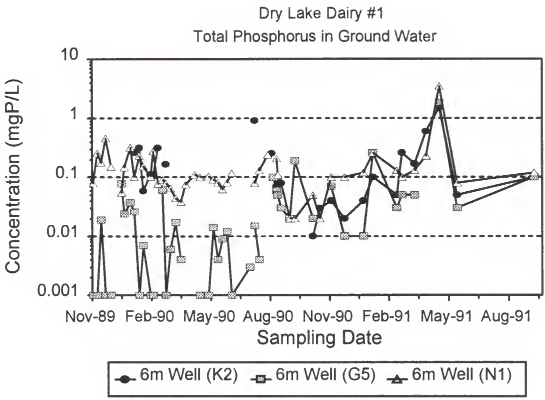

Figure 5-9. Total phosphorus concentration measured in ground water samples from the deep monitoring wells at locations G5, K2 and N1 of Dry Lake Dairy #1.

Table 5-1. Summary of total phosphorus concentrations measured in monitoring wells at each pasture site.

Site	Well Location	Depth meters	Mean TP mgP/L	Number of Samples	Std. Dev. mgP/L
Larson #6	F1m	4	25	37	4.6
	F1s	2	26	32	11
	N1m	4	2.4	49	2.2
W.F. Rucks	G1d	6	0.06	50	0.08
	G1m	3	0.06	47	0.09
	G1s	1	0.22	17	0.21
	M1d	6	0.07	49	0.07
	M1m	3	0.09	37	0.11
	M1s	1	0.12	8	0.05
Williamson	G2d	6	0.09	46	0.09
	G2m	2	0.15	49	0.19
	G2s	1	0.56	10	0.76
	J7m	3	0.05	49	0.06
	J7s	1	0.12	7	0.11
Dry Lake #1	G5d	6	0.07	45	0.27
	G5m	3	0.13	50	0.36
	G5s	1	3.8	5	5.8
	K2d	6	0.22	26	0.33
	K2m	3	0.23	38	0.23
	K2s	1	8.7	11	7.5
	N1d	6	0.21	48	0.49

The very limited shallow water quality data collected at the Williamson site show total phosphorus concentrations generally less than 0.15 mgP/L at 2 meters below the ground surface. Data from the W.F. Rucks site are similar to the observations from Williamson with near surface ground water total phosphorus concentrations in the 0.1 to 1 mgP/L range, decreasing with depth to typically less than 0.1 mgP/L.

Implications of Land Use Intensity

Table 5-2 provides a summary of total phosphorus measurements at each site. In addition to ground water concentrations, measured surface water runoff phosphorus load is presented. These data, collected by Tremwel (1992), give a rough indication of concentration of phosphorus at or near the ground surface or in that shallow ground water leaving the site eventually as surface runoff.

The Larson sites show zero load by definition as no surface runoff occurred. All discharge reaching the stream was derived from groundwater infusion directly to the stream or via seepage faces very near the stream. As can be seen from the table, sites with high land use intensity (cows/ha) demonstrate high concentrations of total phosphorus in the combined ground water and surface water. The distribution between phosphorus in the ground and surface water is related to hydrologic and topographic factors rather than land use intensity.

Table 5-2. Summary of phosphorus concentrations at each investigation site.

Characteristic	Site			
	Larson	Dry Lake	W.F. Rucks	Williamson
Land Use Intensity, cows/ha	18	15	0.6	1
Surface Runoff TP, kgP/ha/yr	0	27	0.9	0.5
Shallow GW TP, mgP/L	30	6	0.2	0.3
Deeper GW TP, mgP/L	10	0.2	0.1	0.1

CHAPTER 6
SUMMARY AND CONCLUSIONS

The objectives set forth in this project were (1) to document the hydrologic processes affecting contaminant transport in the KRBR, (2) to develop techniques and procedures necessary in the study of these processes, (3) to provide estimates of contaminant transport rates and potentials on typical pasture sites of the area by use of tracer studies, and (4) to relate the hydrologic and contaminant transport characteristics to documented phosphorus concentrations in the ground and surface waters of the investigation sites. The extent to which this study addressed these objectives are summarized under three categories: hydrologic, tracer, and ground water quality investigations.

Within the hydrologic investigations are two primary subtopics, water table measurement and water budget. For each of the four study sites, a water table well network was established. These networks permitted the mapping of the water table gradient and the assessment of the influence of various boundary conditions on the subsurface flow patterns. Ground penetrating radar technology was shown to be of limited use in mapping the occurrence and location of the characteristic organic accumulation horizon of spodosols. Deep soil borings proved effective at establishing deep boundary conditions beneath the pasture sites. The borings were also effective in securing samples for assessing vertical distribution of ground water tracers. The investigations into weather, surface runoff and shallow ground water gradients yielded

estimates of water budgets for each site. These water budgets proved to be a good indicator of subsurface flow activity of the sites.

The tracer investigations were divided into two primary sections, the development of sample preparation techniques and the actual tracer experiments into subsurface flow characteristics. The sample preparation effort yielded an effective, efficient procedure to remove nitrate-bromide interferences by inducing denitrification in the stored samples. Two tracer experiments were conducted in this project, one experiment using Rhodamine WT dye to study vertical water movement and one experiment using salt tracers (chloride and bromide) to document both vertical and lateral ground water flow. The dye study was not successful, but the subsequent salt studies did successfully track subsurface flow on the study sites. This produced estimates of ground water flow velocities and also yielded improved methodology for the study of shallow subsurface flow.

The ground water quality investigations included a technology development component (sampling protocol) and phosphorus occurrence and distribution component. The sampling protocol investigation highlighted the dominance of spatial factors over sampling protocol aspects. It also developed and evaluated an effective small-volume sampling device for shallow ground water assessment. The phosphorus assessment component provided strong evidence for a cause and effect relationship between land use intensity and phosphorus concentration in ground water.

When results of the hydrologic, tracer, and water quality investigations are combined, it becomes apparent that topographic features are a good indicator of hydrologic characteristics and thus contaminant transport characteristics. The sites with flat topography (relative to other sites of the region) have a significant surface flow component and low subsurface flow activity. The sites with relatively more surface

slope show little surface flow and much greater subsurface flow activity. The study shows clear partitioning between offsite surface and subsurface phosphorus transport mechanisms based on surface topography and partitioning between high and low offsite loading magnitude based on land use intensity. These results and conclusions contribute to the information base on which agricultural management strategies may be selected and on which water quality management engineering decisions and designs may be considered.

Additional research into contaminant transport mechanisms on flatwoods watersheds will continue and will utilize the extensive database developed during this study. Additional work in computer modeling efforts begun in this project will receive priority. Several factors suggest that modeling efforts will yield practical results. These factors include the apparent strong documented relationships between measurable gross parameters (land use, topography, boundary conditions, etc.) and resultant water flow patterns (surface flow, subsurface flow, and contaminant transport).

Each area of investigation outlined above is presented in slightly more detail in the following sections of this chapter.

Hydrologic Investigations

The hydrologic investigations instituted at the four pasture sites generated a comprehensive data set of reasonably good quality. Detailed hydrologic investigation of remote field sites is a formidable task requiring large amounts of equipment and personnel resources. Various technologies can assist in this task, but they too have their own requirements of time and attention.

Several instruments proved particularly problematic. Among the most difficult to maintain were the pressure sensors installed in selected wells and ditches to provide

continuous water level data. Also difficult to utilize and/or maintain were the ground penetrating radar system, tensiometer systems, the ground water flow meter, and the neutron probe device. Among the more technologically simple monitoring tasks, but equally challenging, were the installation and maintenance of wells, and the boring for deep core samples.

Water Table Measurement

Design of the well networks was based on ground slope and the assumed influence of nearby ditches. However, while surface slope was generally a good indicator of groundwater slope, boundary condition effects were not always dominated by the nearest ditch.

Only at the W.F. Rucks site were ground slope, drainage ditches and deeper water body boundary conditions all aligned to create a common gradient effect. In this case, the water table surface profile was well behaved and perfectly sloped. The Larson site was influenced by a crowning ridge and a water treatment lagoon, both of which introduced a significant lateral component to the water table gradient. The water table at the Dry Lake site showed the influence of a nearby drainage slough. Similarly, the Williamson ground water was affected by a deep drainage canal near the pasture.

Nevertheless, in each of these cases, the network established provided an excellent ability to map the ground water profile of the site. The orthogonal transects proved very important to quantifying lateral components of subsurface flow.

Water Budget

The water budgets calculated for each site appear to correlate with other characteristics and measurements on the sites as described later in the tracer investigations section. These calculations from weather and surface runoff data

provide an excellent indicator of subsurface flow potential as shown in Table 6-1. Water budget calculations accurately identified the Williamson and Larson sites as having the most active subsurface flow systems. The water budget indications of ground water flow correspond with ground water gradient measurements on the study sites. The water budget results also demonstrate that topographic features such as ground surface slope can be useful in identifying which sites will have ground water flow as a major transport mechanism and which sites will have surface runoff as a major transport mechanism. The water budget assessment is confirmed by conclusions from the tracer movement experiments.

Table 6-1. Summary of water budget components over the full period of record.

Component	Water Depth (cm) by Site			
	Larson	Williamson	W.F. Rucks	Dry Lake
Rainfall, cm/yr	93	108	104	113
Pond Seepage, cm/yr	17	N/A	N/A	N/A
Evapotranspiration, cm/yr	83	85	88	90
Surface Runoff, cm/yr	N/A	6	18	25
Net (Subsurface Flow), cm/yr	25	17	-2	-2
Ground Surface Slope, %	1.7	0.42	0.14	0.13
Ground Water Slope, %	1.4	0.4	0.2	0.2

Tracer Investigations

Sample Preparation Techniques

A simple, efficient method to denitrify shallow ground-water samples from high-intensity agricultural areas was developed with the objective of eliminating nitrate interference with ion chromatography (IC) detection of bromide tracers. This was

accomplished while at the same time avoiding any changes to chloride or bromide concentrations.

Biological removal (denitrification) under anoxic conditions offers a simple method with minimal adverse side-effects. Lake sediments serve as the bacteria source enrichment culture prior to use as an inoculant. A 150:1 matrix-inoculant mixture and an overall methanol concentration of 29 mM was sealed and stored in 17 mL assay tubes for 5 days. This procedure was found to provide total denitrification of the ground water matrix in which the initial nitrate concentration measured 240 mg/L NO_3^-. No significant change in either the chloride or bromide concentration was observed. Concentrations of orthophosphate, however, decreased in the samples as a result of calcium precipitation of phosphate induced by pH elevation. In situations where nitrate interference problems exist, anoxic denitrification offers an efficient sample preparation technique for removing nitrate from ground water prior to ion chromatograph analysis for bromide.

Tracer Movement

Bromide was shown to be an effective tracer of shallow ground water movement under the conditions of this investigation. While data collection techniques introduced serious problems in assessing true progress of the tracer, the bromide tracer itself was not the problem. Certain aspects of the tracer investigation remain unexplained, such as the appearance of secondary waves or plumes of bromide. However, this is likely an artifact of actual flow conditions rather than of the particular tracers employed. Chloride can be used successfully as a local tracer. High background levels combined with dilution effects made it impractical as a far-field flow tracer. Standard dye tracers such as Rhodamine WT have even more limited application in the soil environment.

They did not perform well under the conditions of this study. A summary of the results of the lateral tracer experiment is provided in Table 6-2.

The CHEMFLO one-dimensional computer model was shown to generate reasonable estimates of vertical tracer movement during infiltration and migration to the water table. Evaluation much beyond this general statement was not possible due to the problems in data collection methodology as described above. Soils data were assembled for several important regional soil series resulting in creation of "representative" data sets useful for general modeling application.

Table 6-2. Summary of tracer experiment results.

Travel Distance cm	Travel Time (days) by Site			
	Larson	Williamson	Dry Lake	W.F. Rucks
750	80	200	500?	400
1,500	180	400	500?	
3,000	320			
4,500	360			
Plume Speed, cm/hr	0.4	0.16	0.09	0.08
Angle, degrees	45	16	5	24
Adjusted Velocity, cm/hr	0.5	0.16	0.09	0.08

Similarly, simple analytical modeling techniques, such as standard solutions to the advective-dispersive equation, were found to have application to the description of tracer movement results. While application of these models was not possible beyond the calibration step, further research into quantifying appropriate dispersivity values can provide a basis for their application to similar problems. From the model calibration results, lateral dispersivities on these sites were found to be very high relative to

longitudinal dispersivity values. It is believed that this impression was simply imposed by the adverse effects of inappropriate sampling instrumentation as described above.

An interesting observation is made in comparing apparent tracer plume velocity with average water table gradients and with water budget calculations. Both water budget calculations and average water table gradients were good indicators of ground water flow velocity. Of course, gradient data must be combined with soil conductivity information for any rough calculations of flow rates to be made. However reasonable estimates and comparisons of ground water flow can be made without this supplemental information. This suggests that differences in soil properties among these sites are secondary factors to topography and boundary conditions in the process of estimating subsurface flow.

Ground Water Quality Investigations

Sampling Protocol

The results from comparison of monitoring wells and one class of small volume samplers, porous cup samplers, suggest that a rigorous protocol will generate reliable point estimates of nitrogen and phosphorus concentration using either porous cup samplers or monitoring wells. However, neither the porous cup nor the well point estimates are necessarily representative of overall plot or field concentrations. To accurately document shallow groundwater quality on these pasture sites, it appears more important to refine the spatial network (vertical and areal) than to refine the sampling protocol (porous cups vs. wells, number of cup or well volumes, sample preservation, etc.). A rigorous sampling protocol is pointless in the absence of spatial replicates.

The experience of this study clearly shows that in a shallow water table study, use of standard monitoring wells combined with standard sampling protocol is completely inappropriate. Standard monitoring well protocol calls for excavation of three well volumes prior to sampling. In a shallow water table system removal of such relatively large volumes of water from the system can have two primary detrimental effects. First, the volume of water removed can cause significant modification of flow patterns in low gradient situations. This effect is unlikely to be of importance to standard nutrient (nitrogen and phosphorus), monitoring, but is important to spatially sensitive tracer studies. Second, deposition of the excavated water in the soil environment near the monitoring well results in recirculation problems and thus masks the ground water chemical characteristics to be measured. This effect can affect both nutrient and tracer investigations. These recirculation and flow modification problems demonstrate that, for tracer studies in particular, small volume samplers offer a better alternative to standard monitoring wells under conditions similar to this study.

Phosphorus in Ground Water

At Dry Lake, shallow (60 to 100 cm) ground water concentration of phosphorus is on the order of 10 mgP/l. This combined with a tendency to flood and discharge surface runoff provides a high potential for phosphorus discharges. A similar hydrologic potential for phosphorus discharge exists at Rucks. However lower intensity land use offsets this hydrologic factor. The less intense land use is reflected in lower shallow ground water total phosphorus content which seldom exceeds 0.5 mgP/l.

At those sites with greater relief, more rapid ground water flow, and little or no tendency to generate surface runoff (Larson and Williamson), off-site discharge of phosphorus will likely be generated by subsurface drainage to ditches and nearby

natural water bodies. While exhibiting a potential for significant subsurface phosphorus discharge, off-site impacts are minimized as a result of the reduction in phosphorus concentration which occurs as the ground water moves through the soil profile.

At Williamson, shallow (60 to 100 cm) concentrations of 2 mgP/l are reduced to less than 1 mgP/l upon reaching deeper depths (2.5 to 6 meters). Below that depth, a clay horizon both restricts ground water flow and provides a sink for phosphorus. Despite a very dense spodic horizon at the higher elevations of the site which creates a perched water table and standing water at times, rarely did the site generate surface runoff. This characteristic is attributable to the disappearance of a well defined spodic and the perched water table at lower elevations of the site. The water table is also influenced by relatively low drainage boundary conditions induced by nearby ponds and deep drainage ditches.

At Larson, the effects are even more dramatic. In the higher elevations of the site, shallow ground water (2 to 2.5 meters) shows in excess of 40 mgP/l. This concentration decreases to less than 20 mgP/L at greater depths (3 to 4 meters). Yet downslope near the receiving water body (Mosquito Creek) the ground water exhibits less than 2 mgP/l total phosphorus.

Phosphorus Transport Conclusions

Inspection of Table 6-3 suggests several generalizations relating surface/subsurface hydrology to potential for phosphorus transport. It is apparent that topography and drainage boundary conditions play a dominant role in phosphorus transport on these pastures. At all sites, the very shallow (60 to 100 cm) ground water contained much higher levels of phosphorus than deeper ground water (2.5 to 6 meters). The magnitude of the phosphorus concentration appears proportional to land

use intensity. At sites which exhibit low relief, slow ground water flow, and a tendency to generate surface runoff (Rucks and Dry Lake), surface drainage is likely to be a significant transport mechanism for phosphorus.

Given the dramatic differences in water/phosphorus flowpaths, no uniform water management strategy will reduce phosphorus surface and subsurface discharge from these flatwoods pasture sites. Thus, water quality management strategies should be tailored to site specific conditions to be both effective and cost efficient. Data from these four pastures suggest that on extremely flat pastures (slopes less than 0.3%), phosphorus control strategies should emphasize surface flow control or collection/treatment. For pastures with slightly greater slopes (greater than 0.3%), subsurface flow is the primary phosphorus flowpath and local surface water collection/treatment is less likely to yield water quality benefits in the immediate vicinity of the pasture.

Table 6-3. Summary of selected attributes of each investigation site.

Characteristic	**Attribute by Site**			
	Larson	**Williamson**	**W.F. Rucks**	**Dry Lake**
Ground Slope, %	1.7	0.42	0.14	0.13
Surface Runoff, cm/yr	0	6	18	25
Surface Runoff TP, kgP/ha/yr	0	0.5	0.9	27
Water Table Gradient, %	1.4	0.4	0.2	0.2
Plume Velocity, cm/hr	0.5	0.16	0.08	0.09
Subsurface Flow, cm/yr	25	17	-2	-2
Shallow GW TP, mg/L	30	0.3	0.2	6
Deeper GW TP, mg/L	10	0.1	0.1	0.2
Subsurface Flow TP, kgP/ha/yr	25	0.2	0	0
Land Use Intensity, cows/ha	18	1	0.6	15
TP Discharge, kgP/ha/yr	25	0.7	1	27

Surface slope appears to be the primary indicator toward estimating surface runoff potential as demonstrated by Figure 6-1. The flat sites generated more surface runoff than did the sloped sites. This suggests that the real factor which controls surface runoff is subsurface storage. Surface runoff is less important on those sites where significant slope induces significant subsurface flow and thus greater profile storage potential. Topography and boundary conditions dictate subsurface flow which in turn dictates surface runoff.

Figure 6-2 shows that land use intensity is a good indicator of the magnitude of total phosphorus export potential from flatwood pastures. The specific flowpath (surface or subsurface) of the exported phosphorus is a function of the topographic features as shown in Figure 6-1.

As a final note, it is important to recognize that surface runoff is, for flatwoods watersheds, a term defined more by measurement point reference rather than by absolute flowpath. While the bottom of runoff measurement flumes may be at the ground surface elevation or slightly below this elevation (less than 45 cm), the water reaching these flumes may have, at some point in traversing the pasture, experienced contact with shallow portions of the soil profile.

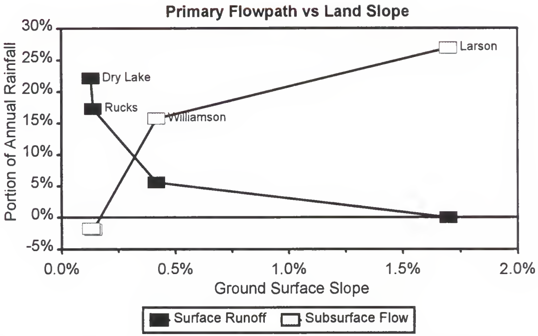

Figure 6-1. Comparison of partitioning between surface and subsurface flow from flatwood pastures as a function of land surface slope.

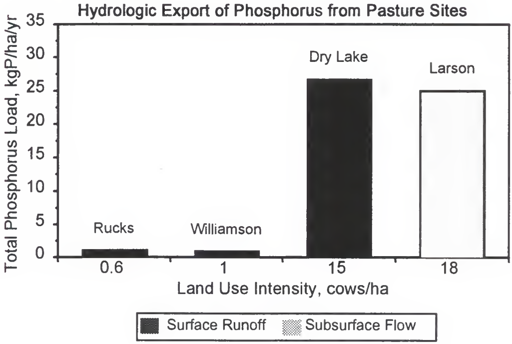

Figure 6-2. Comparison of phosphorus exports from flatwood pastures as a function of land use intensity.

APPENDIX A
SAMPLE PREPARATION TECHNIQUE

The movement of ground water is often documented using bromide tracers combined with ion chromatography detection. This approach, however, can be difficult to apply to shallow ground-water environments beneath high-intensity agricultural areas. Several factors related to the performance of ion chromatographs and the composition of the water samples combine to cause this difficulty.

The Problem

Water samples taken from high-intensity agricultural soils often contain relatively high concentrations of chloride, sulfate, nitrate, and humic substances. These constituents reduce the ability of the ion chromatograph (IC) to quantify the presence of bromide. High concentrations of chloride, sulfate and nitrate can overload the column resulting in reduced chromatograph performance when attempting to detect relatively low concentrations of bromide. Nitrate is a particularly problematic anion due to the close proximity of its IC response peak to that of bromide. Peak separation is not a problem when concentrations of bromide and nitrate are of the same order of magnitude. Increases in ion concentration from a reference level result in a slightly earlier peak appearance. Similarly, decreases in ion concentration from a reference level result in slightly delayed peak appearance. Thus, high nitrate levels (>200 mg/L) and low bromide levels (<2 mg/L) can combine with the other chromatograph

performance problems mentioned to yield nitrate response peaks which either completely obscure or merge with bromide response peaks (see Figure A-1).

Solution Alternatives

This nitrate interference problem must be solved if bromide tracers and ion chromatography detection are to be used effectively to study shallow ground-water movement in high-intensity agricultural areas. A primary limitation on the solution technique is that the method must be easy and inexpensive to apply to a large number of samples, so as to preserve the benefits of using ion chromatography analysis. The solution must also selectively remove nitrate (and possibly sulfate and phosphate), but not significantly modify the bromide or chloride content of the water samples. It is desirable not to modify the chloride concentration in this particular application since chloride is also used as a water movement tracer.

An obvious solution to the problem of bromide tracer detection is to use alternative tracers or alternative detection methods. Ion selective electrodes offer the primary alternative to ion chromatography detection of anions. Electrode detection, however, is subject to interferences from NH_3, Cl^-, I^-, and S^{2-}. Bromide is often selected as a ground-water tracer because of its low background concentrations and relative lack of interaction with other components of the soil-water environment. Bromide is not readily sorbed to soil particles, nor is it taken up in significant quantity by plants -- particularly when sufficient nitrate is present. Iodide is an anion with possible tracer applications. However with standard sodium carbonate/sodium bicarbonate eluants the iodide response peak arrives very late in the ion chromatography procedure. Thus, if iodide tracers were used, the time required for sample analysis would be excessive. Furthermore, iodide can have interference problems with sulfate, which is also present

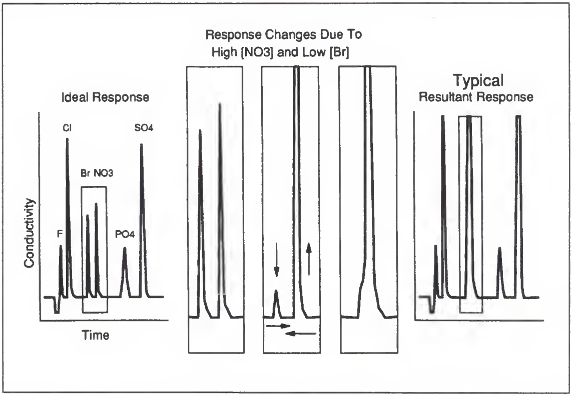

Figure A-1. Ion chromatograph response characteristics resulting from increased nitrate-bromide peak interferences.

in high concentrations in ground-water samples examined. Alternatives to common anion tracers include radioactive isotopes and exotic fluorobenzonates. Both these classes of tracers are prohibitively expensive in both application and analysis. Thus, bromide remains the most practical ground-water tracer.

Given the advantages of using bromide, a possible solution is to use it in sufficient quantities to generate tracer concentrations comparable to, or in excess of background anions. Such a solution would enable samples to be diluted and analyzed without concern for diluting the tracer concentration below the limit of detectability. This solution, however, is not viable for two reasons. First, purchase and application of large quantities is difficult. Furthermore, the objective of the ground-water experiment is to observe the progression of a tracer front. While bromide concentration in the near-field stage of the experiment would be sufficient, dilution in the far-field stage would result in tracer concentrations that are too low. Finally, use of large quantities of bromide tracers have in the past resulted in the death of grazing livestock due to high bromide accumulations in pasture vegetation (Owens et al., 1985).

The accumulation of humic substances in the exchange resin causes a marked reduction in column performance. However it is not a problem which, when solved, will completely eliminate the nitrate-bromide interference problem. A humic-specific guard column can and should be installed in the ion chromatograph to minimize contamination of the separator column by humic substances (Marko-Varga et al., 1984).

A standard technique for the recovery of halogens (Cl^-, Br^-, F^- and I^-) is through precipitation as a silver compound. The precipitated halogens can be collected through filtration and analyzed by the IC after being redissolved using ammonia. In the final analysis, however, the time and effort required for this pre-treatment would be

prohibitive, not to mention the problems posed by the formation of explosive by-products in this procedure (Nechamkin, 1968).

Another method for nitrate removal is reduction to ammonium. Standard wet chemistry nitrogen analysis is based on this process. The standard method involves acidification of the sample followed by the addition of a catalyst (Devarda's alloy) and water bath immersion. While this process is somewhat involved, the main disadvantage is that intolerable quantities of other anions are introduced through the acidification step. The resulting anion concentrations would overload the column making bromide detection impossible. A secondary result would be the complete debilitation of the IC separator column.

Having rejected these various alternatives, we turn to a biological solution. Many species of bacteria are capable of reducing nitrate to gaseous forms of nitrogen (N_20 and N_2). Given a proper understanding of the processes involved, it is a fairly simple task to establish an environment conducive to denitrification, and thus remove the nitrate and eliminate the nitrate-bromide interference problem. It is this alternative which proved to be most effective.

Denitrification

The nitrogen cycle can be examined in the context of the agricultural system from which the water samples are being taken. Nitrogen inputs to the soil water system are in the form of organic nitrogen, ammonium, and nitrate. Sources of ammonium and nitrate nitrogen include fertilizer applications and lightning discharge generation/precipitation. Organic sources include bacterial nitrogen fixation and animal wastes. Cycling of nitrogen within the system begins with the biological decomposition (ammonification) of organic nitrogen and the hydrolysis of urea to ammonium.

Ammonium undergoes biological oxidation to nitrite and ultimately nitrate. This nitrate may be assimilated by vegetation which, in turn, is consumed by livestock. The remaining nitrate is held in the soil-water system.

Nitrogen sinks of the system include ammonia volatilization, denitrification, and animal product exports (milk and meats). Another potential sink is water migration from the site. However on these particular pasture sites surface runoff is an infrequent occurrence and happens only after most surface contaminants have already leached into the soil profile. Ground-water outflow to nearby streams and ditches can also remove nitrate from the system. But given the low relief of these sites and an underlying confining layer, ground-water migration is very slow.

Under anoxic/anaerobic conditions, many species of bacteria are capable of dissimilatory conversion of nitrate to gaseous forms (N_2 and N_2O). These bacteria include the species: Pseudomonas, Achromobacter, Bacillus, and Micrococcus. The bacteria reduce the nitrate as they oxidize carbon sources. Nitrate is used as the terminal electron acceptor of the redox reaction in place of oxygen. Many bacteria also use nitrate in an assimilatory manner, converting nitrate to ammonia which is used in the production of biomolecules. However, the dissimilatory reaction is far more effective at consuming nitrate because it is the primary metabolic pathway for energy production while the assimilatory reaction is only required for production of cell material. The process by which nitrate undergoes conversion to gaseous nitrogen involves several steps as shown in Equation A-1.

Among the factors controlling the rate of this conversion process are: pH, dissolved oxygen, nitrate concentration, and temperature. Mitchell (1974) determined that the optimum temperature for denitrification is 25°C, however significant denitrification can occur at temperatures as low as 5°C. Nelson et al. (1973) indicate

that greater than 50 ppm dissolved organic carbon and less than 1 ppm dissolved oxygen are necessary conditions for denitrification. The optimum pH for denitrification is in the range of 7-8 (Sompongse, 1978). The denitrification rate is much slower under lower pH conditions.

N form:	NO_3^- ------->	NO_2^- ------->	NO ------->	N_2O ------->	N_2	[A-1]
	nitrate	nitrite	nitric oxide	nitrous oxide		
redox :	+5	+3	+2	+1	0	

The fact that the ground-water samples of interest contain very high nitrate concentrations suggests that some factor in the denitrification process is limiting. Denitrifying bacteria are pervasive in the natural environment and would probably be present in sufficient quantity to initiate the process were all other necessary conditions also present. However, the necessary bacteria may not be present in this particular ground-water environment due to other limiting factors. Among the other factors, the requirement of anoxic conditions would be expected to be met in a stagnant ground-water condition (Trudell et al., 1986). The pH level can halt the denitrification process, but for this to occur requires pH less than 3.6. Observed pH on the sites of interest to this study was approximately 6.8. None of these factors (dissolved oxygen, pH or bacterial populations) would appear to be limiting in the pasture water table environment.

The other potential limiting factor is dissolved organic carbon. While the ground-water samples possess a high degree of color from organics, these organics are in the form of humics which are largely unavailable to microorganisms as an energy source. The white to light gray color of the flatwoods soil reflects its low organic matter

content. The spodic horizon and horizons below the spodic appear darker in color suggesting higher organic matter content. Yet these organics may, like the humics, be largely unavailable to the denitrifying bacteria.

When methanol is used as the carbon source for denitrification, the following reaction describes the energy generation process.

$$6NO_3^- + 5CH_3OH \dashrightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad [A\text{-}2]$$

A cell synthesis reaction also affects both the nitrate and methanol consumption rate as described in Equation A-3.

$$3NO_3^- + 14CH_3OH + CO_2 + 3H^+ \dashrightarrow 3C_5H_7O_2N + 19H_2O \quad [A\text{-}3]$$

Combining the synthesis and energy components of the denitrification process yields an overall reaction as presented by Metcalf & Eddy (1979) and shown in Equation A-4.

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow .065C_5H_7O_2N + .47N_2 + .76CO_2 + 2.44H_2O \quad [A\text{-}4]$$

A more complicated thermodynamic analysis of the denitrification process described by Lee (1984), which takes into account cell synthesis, yields a methanol:nitrate mole ratio of 1.13. Experimental results presented by Lee (1984) suggested an even higher methanol:nitrate mole ratio of 1.67. As an explanation for the difference between the thermodynamic value and the experimental value, Lee offers two possible factors. A small portion of the electron donors could be adsorbed to

the solids, or be refractory in nature. Furthermore, oxygen present in the system could react with electrons which would otherwise have been passed to nitrate, thus diminishing the nitrate reduction. In systems with significant aerobic phase, Klapwijk (1983) suggests 1.7 as an appropriate ratio -- which appears to agree with the results of Lee. Metcalf & Eddy (1979) presents a simplified formula for determining the methanol requirement for denitrification, as shown in Equation A-5.

$$C_m = 2.47N_0 + 1.53N_1 + 0.87D_0 \qquad \text{[A-5]}$$

where C_m = required methanol concentration, mg/L
N_0 = initial nitrate-nitrogen concentration, mg/L
N_1 = initial nitrite-nitrogen concentration, mg/L
D_0 = initial dissolved-oxygen concentration, mg/L

Sample Preparation Procedure

The approach taken in developing a practical denitrification procedure was to provide an environment with excess dissolved carbon and inoculate the sample with a denitrifying bacteria source. A methanol solution served as the carbon source and an enrichment culture from lake sediment served as the inoculant source. The ground-water samples which were tested with the denitrification procedure consisted of a composite of samples taken from a dairy pasture. Preliminary analysis revealed nitrate concentrations as high as 500 mg/L NO_3^- in some individual samples prior to their inclusion in the composite sample. Nitrate concentration in the composite ground-water matrix measured 240 mg/L NO_3^-.

Two preliminary experiments were conducted prior to development of a practical denitrification procedure. These experiments employed a glucose carbon solution and

a non-enhanced lake sediment inoculant. This procedure yielded a very slow denitrification rate, requiring 30 days for total nitrate removal.

Table A-1. Composition of mineral solution used for bacterial enrichment.

Compound	Concentration, g/L
$CaCl_2 2H_2O$	16.7
NH_4Cl	26.6
$MgCl_2 6H_2O$	120
KCl	86.7
$MnCl_2 4H_2O$	1.33
$CoCl_2 6H_2O$	2
H_3BO_3	0.38
$CuCl_2 2H_2O$	0.18
$Na_2MoO_4 2H_2O$	0.17
$ZnCl_2$	0.14

Based on results of the preliminary treatment trials, a final denitrification procedure was designed and evaluated. The bacteria inoculant source for the final trial was prepared from bottom sediments taken from Lake Alice on the University of Florida campus. One liter of organic matter and sand was collected from the top 20 cm of bottom sediment which lay beneath 30 cm of water canopied by shoreline trees. The sediment was filtered to remove twigs, leaves and small stones, then mixed in a blender to yield a consistent paste. This paste was diluted with an equal part of deionized water. The mixture was shaken and allowed to settle briefly to remove the sand and large particulates. Bacterial enrichment of the sediment was achieved by adding 2.5 g nitrate, 0.25 g casamino acid, 0.25 g yeast extract, 1.5 g of a mineral solution (Owen et al., 1979) described in Table A-1, and 2 mL methanol.

As the enrichment cycle proceeded, gas generated in the sealed container was bubbled off through a gas trap, thus minimizing oxygen diffusion into the sediment

solution. When the nitrate concentration dropped below 1 mg/L, the heavy sediments were removed by centrifuging at 3000 rpm for 4 minutes. A total of 3 enhancement cycles were applied to the lake sediment prior to its use as an inoculant for the actual experiment. After the final enhancement cycle, the centrifuged sediments were re-suspended in deionized water and again centrifuged. This procedure was repeated twice to remove all readily soluble components (chloride, sulfate, phosphate, etc.).

The samples subjected to the denitrification treatment consisted of three matrix types: 1) a composite ground-water sample matrix from a pasture site under investigation with chloride, bromide, nitrate, phosphate, and sulfate concentrations of 29, 4, 240, 87 and 140 mg/L, respectively; 2) a standard matrix prepared from deionized water combined with potassium and sodium salts of chloride, bromide, nitrate, phosphate, and sulfate to concentrations of 100, 5, 300, 100 and 100 mg/L of these anions, respectively; and 3) a deionized water matrix. The pre-treatment nitrate:bromide concentration ratio was below 100:1 which is the approximate interference threshold.

Treatment of the three matrix types consisted of adding 0.1 mL of enhanced inoculant and 0.1 mL of 20% methanol solution. Untreated control samples were also prepared for parallel analysis. The treated samples were stored in capped, 17 mL vials. A total of 32 replicates were prepared of each treated matrix. In preparing the samples, the prescribed volume of methanol was first placed in the vials, followed by the standard solutions, and last the inoculant volume. This procedure avoids exposing the inoculant to localized high concentrations of methanol which would be toxic to the bacteria.

The methanol:nitrate ratio in Equation A-4 is 1.08. A higher ratio (1.7) is suggested by the results of investigations previously cited (Lee, 1984). For a 300 mg/L

nitrate sample, the 0.1 mL, 20% methanol quantity used in the experiment represents a methanol:nitrate mole ratio of 6. This is greatly in excess of the 1.7 ratio suggested by Lee.

Each day after preparation of the treated samples, 3 replicates were randomly selected and combined. The composite sample was passed through a 0.45 micron filter. The filtered sample was analyzed using a DIONEX QIC Ion Chromatograph equipped with an NG-1 humics guard column, an AG4A concentrator column, an AS4A anion separator column and a conductivity cell detector. The eluant consisted of 2 mM Na_2CO_3 and 4 mM $NaHCO_3$ solution pumped at a rate of 1.5 mL per minute. A 0.25 mM H_2SO_4 solution with a flow rate of 3 mL per minute served as the suppressor regenerant.

Method Evaluation

Recovery results for chloride, bromide, nitrate, phosphate and sulfate are presented in Figures A-2 to A-6. Results show that both the ground-water and standard matrix samples were completely denitrified within a few days after treatment. The nitrate concentration in these two samples decreased at a rate of 2.9 mg/L-hr and 2.0 mg/L-hr, respectively.

Bromide and chloride concentrations were not significantly affected by the denitrification treatment. The only constituent which showed significant deviation from the untreated samples was the phosphate content of the ground-water matrix samples. The phosphate concentration in these samples declined at a rate of 0.35 mg/L-hr during the period of denitrification (0-84 hours). The treated standard samples did not show any significant decline in phosphate content. The difference between the phosphorus recovery rate for the ground-water matrix and standard matrix can be

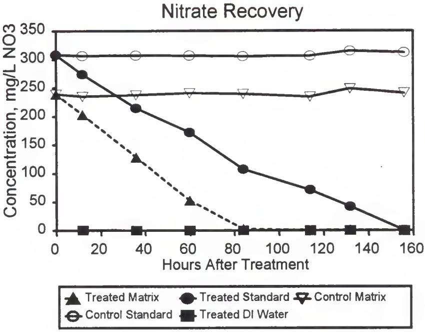

Figure A-2. Results of nitrate recovery analyses for denitrification experiment treatments.

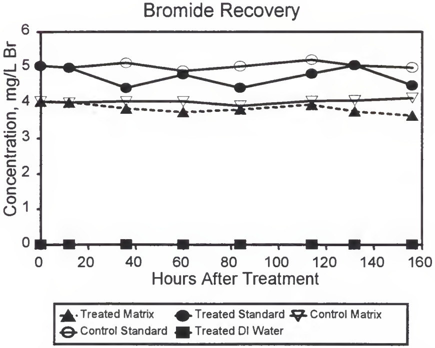

Figure A-3. Results of bromide recovery analyses for denitrification experiment treatments.

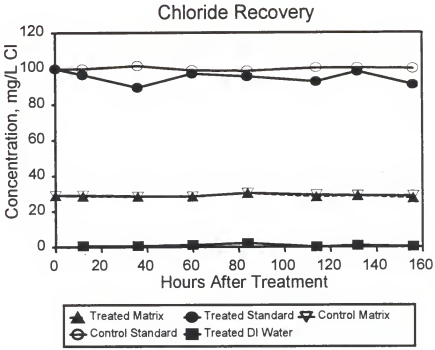

Figure A-4. Results of chloride recovery analyses for denitrification experiment treatments.

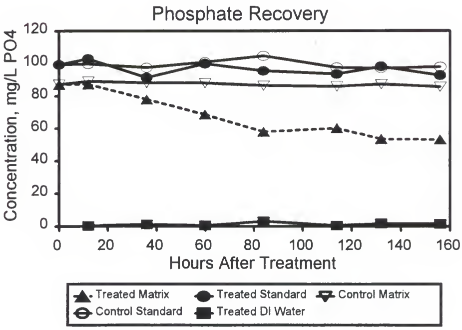

Figure A-5. Results of phosphate recovery analyses for denitrification experiment treatments.

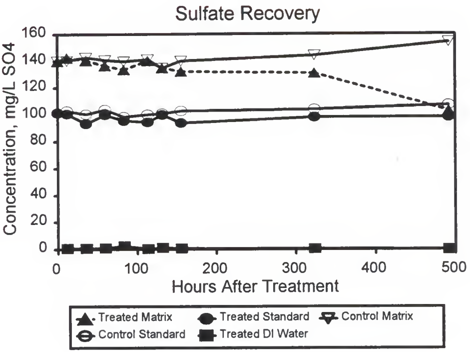

Figure A-6. Results of sulfate recovery analyses for denitrification experiment treatments.

attributed to precipitation as calcium phosphate resulting from changes in pH. Untreated sample pH was 6.8 for the ground-water matrix and 7.7 for the standard matrix. After denitrification the pH measured 7.8 for both the ground water and standard. In moving from a pH of 6.8 to 7.8, iron and aluminum species of phosphate become more soluble while calcium species of phosphate become less soluble. After a long period under tightly sealed conditions, the ground-water matrix samples did appear to attain a sufficiently low redox potential such that sulfate conversion to hydrogen sulfide became possible. The last point of the treated matrix data (hour 492) supports this assessment (see Figure A-6). Sulfate removal would be expected to become significant if treated ground-water samples are stored for more than two weeks.

Method Summary

When present in extremely high concentrations, nitrate has the potential to interfere with ion chromatography detection of bromide tracers. This situation is unlikely to occur unless nitrate concentrations exceed bromide concentrations by two orders of magnitude. While unusual, this situation does occur under high-intensity agricultural conditions. Standard methods for the removal of nitrate from these problematic ground-water samples are either not viable due to the modification of other anion concentrations or are not practical due to the high labor inputs required.

In situations where nitrate interference problems exist, anoxic denitrification offers an efficient sample preparation technique for removing nitrate from ground water prior to ion chromatograph analysis for bromide. Through the addition of small quantities of a methanol carbon source and inoculation with an enhanced bacteria source, large numbers of samples can be treated to remove nitrate interference

problems in a few days. This treatment technique causes no significant changes in chloride or bromide concentrations, but can alter other constituents such as phosphate and sulfate. If anaerobic conditions are allowed to persist after the denitrification process is completed, then the redox potential will become sufficiently low that sulfate will be converted to hydrogen sulfide and released. Phosphate precipitation can be expected in the samples as a result of changes in sample pH.

APPENDIX B
GROUND WATER SAMPLING PROTOCOL

During the past few years Florida governmental agencies have instituted ground water quality monitoring requirements for all dairy farms in the Lake Okeechobee area. This action was undertaken as part of an overall program to address water quality problems of the south Florida region, which includes the Kissimmee River, Lake Okeechobee and Florida Everglades. As with all new monitoring programs, these shallow ground water observations began in the context of limited understanding of the site-specific conditions. Thus, appropriate sampling protocol and interpretation guidelines are still evolving. Current regulatory guidelines stipulate that total phosphorus concentrations in groundwater meet certain criteria. However there exists little historical data on reproducibility or spatial variability important to the interpretation of such monitoring results.

Some of the first observation wells installed as part of this dairy pasture study attempted to sample a large depth range. The wells were continuously screened from within a few feet of the surface to a depth of thirty or more feet. Experience quickly pointed out several inadequacies of this system. Problems such as vertical concentration gradients and preferential recharge of the wells caused all parties involved to view the sampling results with skepticism. One particularly serious problem arises because of recirculation between the well and waste well water dumped on the ground surface near the well. The waste well water is generated in the process of following accepted sampling protocol (removal of at least three well volumes prior to sample removal).

These questions surrounding sampling methodology and results interpretation led area farmers, represented by the Florida Dairy Farmers, Inc., to seek additional information and alternatives. Among the ideas considered was to retrofit the existing wells to limit the depth range from which the samples were drawn. Other alternatives included installation of new sampling systems (multilevel samplers, wells with more limited screen lengths, or solution samplers fabricated using porous ceramic cups). In addition to being of direct interest to area farmers, the need to explore alternative sampling instrumentation and methodology became critically apparent in the course of undertaking the tracer experiments described in this document. Wells presented too many limitations for sampling tracers in the shallow ground water environments. A better technique needed to be developed and implemented.

To compare the appropriateness of two of these alternatives (wells and porous cup samplers), an experiment was implemented on three of the four pasture sites (Larson, Williamson and Rucks). The investigation compared porous cup solution samplers and screened PVC wells in sampling shallow ground water for nitrogen and phosphorus.

Sampling Techniques

The most commonly-employed soil solution samplers are those which use porous ceramic cups or cylinders. Monitoring wells are still the most often used method for sampling the saturated zone. The ground water monitoring industry is well established and, thus, has developed a fairly comprehensive set of guidelines for well installation and sampling protocol. These guidelines are outlined in a variety of ground water handbooks. Porous ceramic cup samplers are not employed as extensively as

are wells. Their usage is generally limited to the academic domain. Accordingly, guidelines for their application are less well established and subject to more debate.

Linden (1977) presents an introduction to ceramic samplers in his U.S. Department of Agriculture technical bulletin. Linden describes a protocol for the construction and use of these samplers. Grossmann and Udluft (1991) also provide an in-depth review of the suction-cup sampling method. Their review includes preparation, installation, spatial variability, and other sub-topics. A variety of authors have offered guidelines for the application of porous cup samplers: Litaor (1988), Hughes and Reynolds (1988), Nagpal (1982), Debyle et al. (1988), Silkworth and Grigal (1981), Hansen and Harris (1975).

Most questions surrounding porous cup sampling techniques deal with whether or not these samples are representative of the actual soil solution. A common recommendation is to allow samplers to equilibrate with the surrounding soil for an appropriate period of time before sampling (Hughes and Reynolds, 1988; Litaor, 1988). Many authors also suggest discarding the initial samples and retaining only the last of several sequential samples for analysis (Nagpal, 1982; Hughes and Reynolds, 1988; and Debyle et al., 1988). Despite these sampling protocol suggestions, other factors have led investigators to conclude that only relative, not quantitative, results can be expected from this technique (Barbarick et al., 1979; Van De Pol et al., 1977; and Biggar and Nielsen, 1976)

One problem cited by investigators is the interaction between the ceramic cup material and the soil solution constituents (Rauland-Rasmussen, 1989; Debyle et al., 1988; Creasey and Dreiss, 1988; Bottcher et al., 1984; Nagpal, 1982; Zimmermann et al., 1978; and Hansen and Harris, 1975). Sorption appears to be a greater problem for calcium, aluminum, potassium and phosphate, and a lesser problem for nitrate.

Another area of study is the effect of sampling time and sampling suction. Sampling time can affect the sorption equilibrium, while sampling suction can affect the distribution of pore sizes from which the sample is drawn (Morrison and Lowery, 1990a; Morrison and Lowery, 1990b; Debyle et al., 1988; Ranson and Smack, 1986; Nightingale et al., 1985; Warrick and Amoozegar-Fard, 1977; Severson and Grigal, 1976; Hansen and Harris, 1975; England, 1974; and Wood, 1974). Exposing samples to suctions can also alter the water chemistry through carbon dioxide degassing (Suarez, 1987).

Beyond the question of whether or not the porous cup sample is representative of the soil solution lies the question of whether the soil solution at any given point is representative of the entire site. The problem of spatial variability has been addressed in a number of investigations (Pedersen et al., 1991; Krajenbrink et al., 1988; Anderson, 1986; Van Luik and Harrison, 1984; Shaffer et al., 1979; Alberts et al., 1977; and Hansen and Harris, 1975). Nitrate was the most commonly studied constituent. Reported coefficients of variation ranged from 0.1 to 0.7, with most falling below 0.4. Results of these studies point out that a large number of sample replicates are required if the investigator seeks to assign any reasonable statistical significance to reported mean values.

In an effort to develop improved sampling methods, porous cups have been compared against other devices such as pan samplers, zero-tension lysimeters, and hollow fiber lysimeters (Rasmussen et al., 1986; Barbee and Brown, 1986; Haines et al., 1982; and Levin and Jackson, 1977). While differences due to samplers were often observed, porous ceramic still seems to enjoy wide-spread acceptance in the scientific community.

Periodically, new solution sampler designs are developed and published. Some of these are for specialized applications, while others are intended for general unsaturated or saturated application. Among the saturated zone samplers developed in recent years are those by Morrison and Szecsody (1985), Galgowski and Wright (1980), Sondergaard (1990), Picken et al. (1978), and Hansen and Harris (1974). Unsaturated/saturated designs include those by Suarez (1986), Nightingale et al. (1985), Morrison (1982), Knighton and Streblow (1981), Wood et al. (1981), Harris and Hansen (1975), and Wood (1973).

Experimental Procedures

In 1990, a total of eight porous ceramic cup solution samplers were installed on three of the four sites. Schematics of the wells and the solution samplers are provided in Figure B-1. A more detailed diagram of the porous cup groundwater sampler is shown in Figure B-2. Both the monitoring wells and the porous cup samplers were constructed using 5-cm, schedule 40 PVC pipe and fittings.

The solution samplers used in this study were composed of a sampling chamber, an extension pipe assembly, and two polypropylene tubes which connect the chamber to the ground surface. The chambers are assembled in the lab and are fitted with the tubes and extension pipe in the field immediately prior to installation. The monitoring wells have a silica sand filter pack, while the porous cup samplers are surrounded by natural backfill. Porous cup samplers were positioned approximately 1.5 meters from the corresponding monitoring well. The porous cups were installed at a depth equal to the middle of the screened section of the corresponding monitoring well. Table B-1 describes each monitoring well and porous cup groundwater sampler.

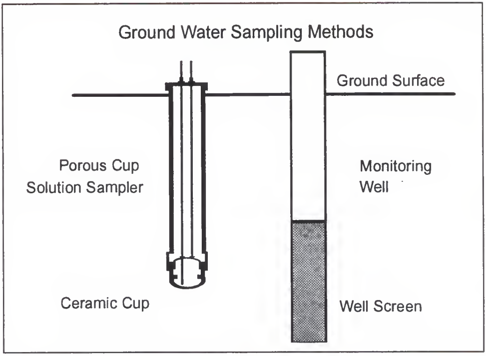

Figure B-1. Comparison of porous cup solution sampler and monitoring well systems for sampling ground water.

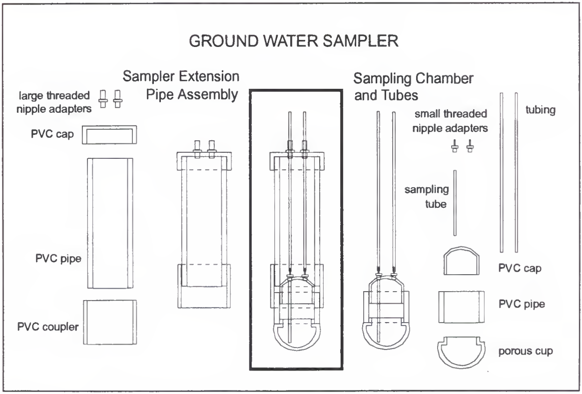

Figure B-2. Components and assembly of porous cups solution sampler for monitoring ground water.

Table B-1. Specifications of wells and porous cup samplers. Distances are given as meters below the ground surface.

Site	Station I.D.	Well Screen (meters)	Porous Cup (meters)
Larson Dairy	F1m	2.5 to 4.6	3.5
Larson Dairy	N1m	1.7 to 3.0	2.3
Rucks Dairy	G1m	1.9 to 3.2	2.6
Rucks Dairy	G1d	4.4 to 6.0	5.2
Rucks Dairy	M1m	1.5 to 2.7	2.1
Williamson Ranch	WQ1m	2.4 to 3.7	3.1
Williamson Ranch	WQ1d	4.5 to 6.0	5.3
Williamson Ranch	WQ2m	2.1 to 3.0	2.6

The porous cup chambers were constructed to accomodate a 250 mL sample. After installation, the tops of the extension pipes were protected from livestock using a shelter constructed from 60-cm sections of 46-cm PVC pipe. These shelters were fixed in the ground with concrete and covered by a hinged wooden panel. Ends of the polypropylene tubes were covered with rubber tips to discourage ants from using the tubes as residential wells.

In sampling the porous cup samplers, vacuum was applied to a flask connected to the tube extending to the bottom of the chamber (see Figure B-3). To refill the chamber after sampling, the sampling tube valve was closed and vacuum was applied to the chamber vent tube. A small hand suction pump was employed to generate a chamber pressure of approximately 20 kPa. Once the chamber and tubes had filled and water was visible in the tubing above the ground surface, the chamber was again sampled.

Performance of the sampling chamber porous ceramic cups were tested in the laboratory prior to installation to assess mixing and phosphorus sorption characteristics.

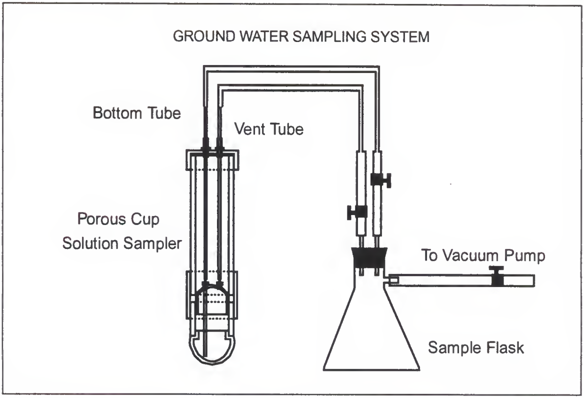

Figure B-3. Sampling technique for porous cup solution samplers.

This was accomplished by placing the chambers in a bath of 1 mgPO4/L standard solution and placing a suction on the cup, extracting sequential samples until equilibrium was achieved. Then with the chamber empty, the standard solution was changed to deionized water for the "step-down" test. A series of samples representing sequential chamber volumes were then extracted and tested for phosphate content. After equilibrium had again been achieved, the deionized water was replaced with the 1 mg/L standard solution for the "step-up" test. Two step-up and two step-down tests were performed.

In the field environment, inducing flow by reducing the sample chamber pressure can cause sample degassing and, thus, changes in sample pH as described by Suarez (1986). Use of a limited-volume sample chamber can be helpful in reducing pH errors due to degassing (Suarez, 1986). Also, interaction between the atmosphere and the soil environment surrounding the sample chamber can be eliminated by leaving the sample chamber and tubes filled and sealed between sampling dates.

The porous cup sampling procedure was repeated five or more times for each of seven locations. One sampler (WFR M1m) appeared to have become clogged by fine soil particles. Its sampling rate (less than 100 mL/hr) was too slow to permit repeated sampling. The amount of time required to fill the chambers for each sampler varied due to differences in soil texture. Each sample was immediately filtered through a 0.45 um membrane, and half was treated with sulfuric acid to reduce the pH to less than 3.0. Both the acidified and non-acidified samples were then refrigerated and transported to the laboratory for analysis. Immediately after the porous cups were sampled, the monitoring wells were also sampled. A stainless steel bailer with a diameter of 3.8 cm and a capacity of 750 mL was used. A series of five samples were taken from the wells

in succession, after removing 0, 1, 3, 4 and 6 casing volumes from the well. The resulting well samples were handled identically to samples from the porous cups.

Results

The porous cup manufacturer claims that the material currently used in the manufacture of the ceramic cups is more inert to phosphorus as compared to ceramics used in previous years. However, results of preliminary lab tests of the newly manufactured cups (shown in Figure B-4 and Figure B-5) were very similar to measurements by Bottcher et al. (1984). While the new cups may be marginally improved over older versions, they seem to perform similarly to the older cups for practical purposes. Initial laboratory tests do not, however, say much about differences in cup performance which may become apparent over the long term following installation in the soil environment.

The step-up and step-down tests of the ceramic cups do not distinguish mixing effects from phosphate sorption effects. As seen in Figure B-4, the sampling chamber phosphate concentration approached zero very quickly in the step-down test (1 mg/L to 0 mg/L). By the second chamber volume, the concentration had already covered 95% of its full step change. In the step-up test (Figure B-5), chamber sample phosphate concentrations reached that of the standard on the second chamber volume. However, in the third and fourth chamber volume, the concentration actually exceeded that of the standard, indicating a sorption/desorption process between the standard solution and the ceramic material.

The groundwater samples taken from both the monitoring wells and the solution samplers were analyzed for total phosphorus (TP), soluble reactive phosphorus (SRP),

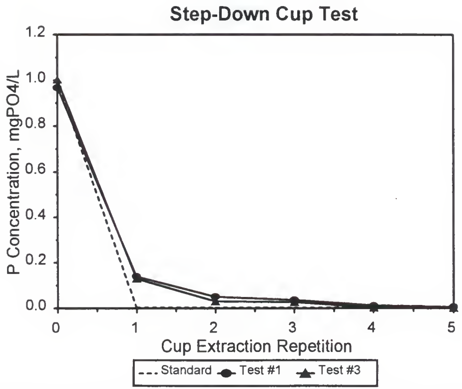

Figure B-4. Step-down test results for porous ceramic interaction with phosphate.

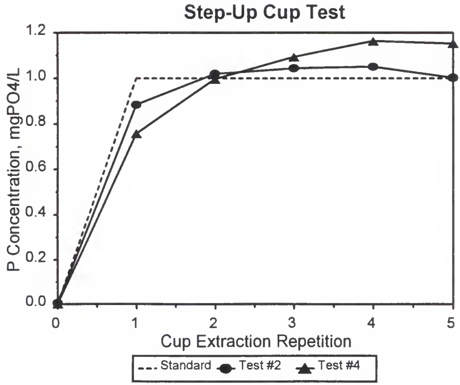

Figure B-5. Step-up test results for porous ceramic interaction with phosphate.

total kjeldahl nitrogen (TKN), and nitrate (NO_3). Both acidified and non-acidified samples were tested.

Tests showed the acidified samples to have slightly higher TKN and NO3 values than the non-acidified samples. The mean differences were 0.08 mgN/L and 0.003 mgN/L , respectively. The paired observations were evaluated and the difference was found not to be significantly different from zero at the alpha equals 0.05 level. TP and SRP values were also slightly higher for the acidified samples. The mean concentration differences of 0.14 mgP/L and 0.81 mgP/L, respectively, were significantly different from zero indicating that the acid treatment did affect the TP results. Tables B-2 through B-7 present the data for each nutrient parameter. Results for TP, NO_3, and TKN reflect acidified sample concentrations. Acidified SRP concentrations were not well behaved and may be flawed. This may, in part, be due to the long lag (30 days) between sampling and analysis dates.

The mean concentrations from the porous cup samples and the monitoring wells were compared to determine whether these values were statistically different from one another. First, means and standard deviations were determined using the last four samples taken at each sampling device. Small-sample confidence intervals were determined using the last four samples taken at each sampling device. Confidence intervals were determined for each mean concentration. Many of the sampling sites showed statistically significant difference between the well and the porous cup sampler mean concentrations (see Table B-8). The test results were further examined to determine whether these differences could be quantified as a cup/well effect. Mean values were calculated using results from the last two samples from each device (the 4th and 5th cup volume and the 4th and 5th well volumes). Paired observation tests showed that the differences observed between SRP, TP and TKN concentrations from

Table B-2. Total Kjeldahl Nitrogen results for sequential ground water sampling from porous cup solution samplers.

Site	Location	TKN, mgN/L				
		Cup 1	Cup 2	Cup 3	Cup 4	Cup 5
Larson	F1m	17	16	16	17	17
	N1m	1.6	1.6	1.6	1.7	1.6
Williamson	G2d	2.5	2.4	2.4	2.4	2.4
	G2m	5.8	6.4	6.6	6.5	6.6
	J7m	1.9	1.4	1.4	1.3	1.3
W.F. Rucks	G1m	2.3	2.1	1.7	1.6	1.6
	G1d	2.1	1.7	1.5	1.4	1.5
	M1m	2.9	3.1	2.1	2.7	3.1

Table B-3. Total Kjeldahl Nitrogen results for sequential ground water sampling from monitoring wells. Samples were taken immediately following the removal of 0, 1, 3, 4, and 6 well volumes.

Site	Location	TKN, mgN/L				
		Well 0	Well 1	Well 3	Well 4	Well 6
Larson	F1m	14	15	16	16	15
	N1m	5.7	6.1	5.7	5.7	5.7
Williamson	G2d	2.7	2.8	2.7	2.7	2.6
	G2m	7.5	7.3	5.3	4.9	4.5
	J7m	1.4	1.9	1.7	1.6	1.6
W.F. Rucks	G1m	1.4	1.6	1.4	1.5	1.4
	G1d	1.2	1.2	1.1	1.1	1.1
	M1m	1.9	1.7	1.6	1.8	1.8

Table B-4. Total Phosphorus results for sequential ground water sampling from porous cup solution samplers.

Site	Location	TP, mgP/L				
		Cup 1	Cup 2	Cup 3	Cup 4	Cup 5
Larson	F1m	30	28	29	29	29
	N1m	0.41	0.27	0.31	0.27	0.25
Williamson	G2d	1.7	0.24	0.11	0.22	0.21
	G2m	0.97	1.1	1.2	1.2	1.2
	J2m	0.09	0.12	0.21	0.16	0.28
W.F. Rucks	G1m	0.21	0.06	0.12	0.21	0.11
	G1d	0.06	0.08	0.06	0.09	0.06
	M1m	0.03	0.03	0.01	0.03	0.02

Table B-5. Total Phosphorus results for sequential ground water sampling from monitoring wells. Samples were taken immediately following the removal of 0, 1, 3, 4, and 6 well volumes.

Site	Location	TP, mgP/L				
		Well 0	Well 1	Well 3	Well 4	Well 6
Larson	F1m	24	36	37	37	35
	N1m	9.6	8.4	7.6	7.7	7.5
Williamson	G2d	0.06	0.43	0.18	0.08	0.04
	G2m	0.41	0.21	0.18	0.79	0.62
	J7m	0.32	0.11	0.09	0.04	0.09
W.F. Rucks	G1m	0.09	0.06	0.09	0.09	0.09
	G1d	0.06	0.03	0.01	0.05	0.05
	M1m	0.05	0.12	0.09	0.03	0.12

Table B-6. Nitrate results for sequential ground water sampling from porous cup solution samplers.

Site	Location	NO_3, mgN/L				
		Cup 1	Cup 2	Cup 3	Cup 4	Cup 5
Larson	F1m	0.32	0.82	0.76	0.78	0.70
	N1m	0.46	0.01	0.01	0.01	0.01
Williamson	G2d	0.19	0.00	0.00	0.00	0.00
	G2m	0.00	0.02	0.00	0.00	0.00
	J2m	0.00	0.04	0.00	0.02	0.00
W.F. Rucks	G1m	0.00	0.01	0.00	0.00	0.00
	G1d	0.01	0.01	0.01	0.01	0.01
	M1m	0.00	0.01	0.01	0.00	0.01

Table B-7. Nitrate results for sequential ground water sampling from monitoring wells. Samples were taken immediately following the removal of 0, 1, 3, 4, and 6 well volumes.

Site	Location	NO_3, mgN/L				
		Well 0	Well 1	Well 3	Well 4	Well 6
Larson	F1m	0.11	0.03	0.01	0.01	0.01
	N1m	0.07	0.01	0.02	0.07	0.19
Williamson	G2d	0	0.08	0.03	0.03	0.04
	G2m	0.02	0.04	0.02	0.05	0.01
	J7m	0.02	0.01	0	0	0.01
W.F. Rucks	G1m	0	0	0	0	0
	G1d	0.12	0.01	0	0	0
	M1m	0.09	0.04	0.01	0	0

Table B-8. Comparison of porous cup sampler and monitoring well mean concentration values for each parameter and each sampler location.

Site	Location	TKN	TP	NO_3	SRP
Larson	F1m	S	S	S	S
	N1m	S	S	NS*	S
Williamson	G2d	S	NS	S*	NS*
	G2m	NS	S	S*	S
	J7m	S	S	NS*	NS
W.F. Rucks	G1m	S	NS*	NS*	NS*
	G1d	S	S*	S*	NS*
	M1m	S	S*	NS*	S*

S indicates significantly different concentration means.
NS indicates not significantly different concentration means.
* Indicates that the confidence interval is very near the parameter minimum detection limit.

the porous cups and monitoring wells were not significantly different from zero (at the alpha = 0.05 level). There was a significant difference in NO_3 concentrations between the two devices. The porous cups yielded samples with an average nitrate concentration 0.07 mgN/L greater than samples taken from the well. However the confidence interval for this mean difference extended down to 0.02 mgN/L, which is well within the analysis error.

The observed differences between the two devices could not be quantified as a consistent cup/well effect. Rather, the difference appears to be simply an artifact of spatial variability of the nitrogen and phosphorus concentrations between the porous cup and well sampling points. This spatial effect may include the effect of vertical integration which occurs in the monitoring wells. While the spatial effect may be as high as 100% between samplers located within only a meter of one another, results from other sampling points located on the same site show much greater variability. The multiple sampling points on a site may be separated by as much as 200 meters and were accompanied by changes in soil type.

The results were also examined from the perspective of establishing an appropriate sampling protocol for each device. Figures B-6 through B-9 compare the concentrations of the sequence of samples to the concentration of the last sample taken from a well or cup sampler. These results show that the porous cup sample concentrations converged more rapidly than concentrations in the well samples.

Results of the protocol evaluation suggest that porous cup samplers can be problematic due to the long time required to secure two sequential samples after first emptying the porous cup chamber. This process can take 15 to 30 minutes. Given the need to minimize pH errors induced by degassing, a practical sampling method might be as follows. First, the old chamber water is removed. Next, suction is applied to a

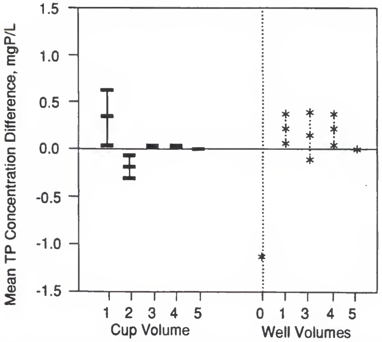

Figure B-6. Comparison of porous cup sampler and monitoring well convergence toward final total phosphorus concentration. Plotted are the differences and confidence intervals between the sequential samples mean concentration for all locations and the final (5th) mean concentration.

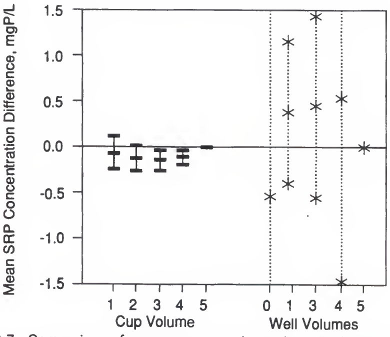

Figure B-7. Comparison of porous cup sampler and monitoring well convergence toward final soluble reactive phosphorus concentration. Plotted are the differences and confidence intervals between the sequential samples mean concentration for all locations and the final (5th) mean concentration.

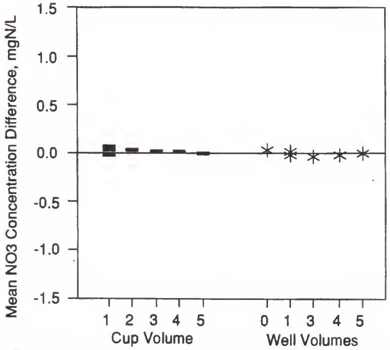

Figure B-8. Comparison of porous cup sampler and monitoring well convergence toward final nitrate concentration. Plotted are the differences and confidence intervals between the sequential samples mean concentration for all locations and the final (5th) mean concentration.

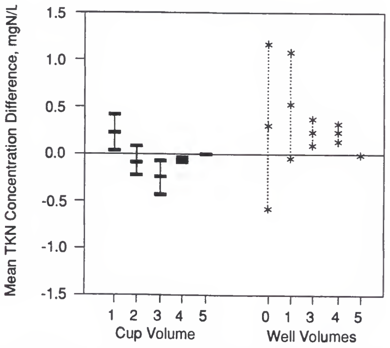

Figure B-9. Comparison of porous cup sampler and monitoring well convergence toward final total kjeldahl nitrogen concentration. Plotted are the differences and confidence intervals between the sequential samples mean concentration for all locations and the final (5th) mean concentration.

sealed sample flask with the vent tube and sampling tube valves open to the sample chamber. Once the desired flask pressure has been attained, the sampling tube valve is closed while the vent tube valve is left open. This should isolate a small amount of water in the sampling tube and induce water to fill the chamber then rise up the vent tube and drip into the sample flask. If the sealed vacuum flask is left to draw water until at least 250 mL (one chamber volume) has collected, then the water remaining in the porous cup chamber will represent the third cup volume. Furthermore, this third cup volume would be reasonably isolated from the large volume of low pressure air in the flask and, therefore, would not suffer significant degassing (Suarez, 1987). After the flask is opened and emptied, the third cup volume can be quickly removed from the chamber, filtered, preserved, refrigerated and retained for analysis.

Given that shallow groundwater wells can experience water recirculation problems and given that the porous cup samplers produced nitrogen and phosphorus concentration results similar to monitoring wells, small-volume sampling techniques appear more appropriate for this particular application. The porous cup sampler design used in this study presents a viable alternative to wells. However, other sampler designs may be preferable alternatives. Various small-volume groundwater sampler designs (described above) offer multi-level sampling capabilities, and with a little effort, these small-volume samplers can also be used as piezometers (Picken et al., 1978).

Protocol for nitrogen and phosphorus sampling from monitoring wells includes removal of at least 3 well volumes prior to securing a test sample. For porous cup samples, the second or third cup volume (first or second sample after removing the old standing water) should provide a locally representative sample. Both sampling techniques generated concentration values with an approximate standard deviation of 10% or 0.15 mgN/L (whichever is greater) and 5% or 0.05 mgP/L (whichever is

greater). Sample acidification is important for accurate phosphorus concentration results, but not significant for nitrogen.

As for the questions raised by the Florida Dairy Farmers, Inc., results of this study suggest that retrofitting existing wells is a viable option. Wells retrofitted with porous ceramic cups or cylinders could be expected to yield representative samples. Samples with point replicate coefficients of variation of 10-20% can be obtained. However, average point concentrations may differ from nearby point concentrations by more than 100%. Therefore, recommendations for shallow groundwater sampling networks on similar south Florida pasture sites should stress spatial factors, rather than protocol factors.

These results suggest that a rigorous protocol will generate reliable point estimates of nitrogen and phosphorus concentration using either porous cup samplers or monitoring wells. However, neither the porous cup nor the well point estimates are necessarily representative of overall plot or field concentrations. To accurately document shallow groundwater quality on these pasture sites, it appears more important to refine the spatial network (vertical and areal) than to refine the sampling protocol (porous cups vs. wells, number of cup or well volumes, sample preservation, etc.). A rigorous sampling protocol is pointless in the absence of spatial replicates.

BIBLIOGRAPHY

Abdalla, N.A. and B. Lear. 1975. Determination of inorganic bromide in soils and plant tissues with a bromide selective ion-electrode. Communications in Soil Science and Plant Analysis, 6: 489-494.

Alberts, E.E., R.E. Burwell, and G.E. Schuman. 1977. Soil nitrate-nitrogen determinant by coring and solution extraction techniques. Soil Science Society of America Journal, 41: 90-92.

Anderson, L.D. 1986. Problems interpreting samples taken with large-volume, falling-suction soil-water samplers. Ground Water, 24(6): 761-769.

Barbarick, K.A., B.R. Sabey, and A. Klute. 1979. Comparison of various methods of sampling soil water for determining ionic salts, sodium, and calcium contents in soil columns. Soil Science Society of America Journal, 43:1053-1055.

Barbee, G.C. and K.W. Brown. 1986. Comparison between suction and free-drainage soil solutions samplers. Soil Science, 141(2): 149-154.

Bathke, G.R., D.K. Cassel, and P.A. McDaniel. 1992. Bromide movement at selected sites in a dissected piedmont landscape. Journal of Environmental Quality, 21: 469-475.

Biggar, J. W. and D. R. Nielsen. 1976. Spatial variability of the leaching characteristics of a field soil. Water Resources Research, 12: 78-84.

Bottcher, A.B., L.W. Miller, and K.L. Campbell. 1984. Phosphorus adsorption in various soil-water extraction cup materials: effect of acid wash. Soil Science 137(4): 239-244.

Bowman, R.S. 1984. Evaluation of some new tracers for soil water studies. Soil Science Society of America Journal, 48: 987-993.

Butters, G.L., W.A. Jury, and F.E. Ernst. 1989. Field scale transport of bromide in an unsaturated soil: 1. Experimental methodology and results. Water Resources Research, 25(7): 1575-1581.

Campbell, G.S. 1985. Soil physics with basic transport models for soil-plant systems. Elsevier, New York, NY.

Capece, J.C., K.L. Campbell, and L.B. Baldwin. 1986. Estimation of runoff peak rates and volumes from flatwoods watersheds. Final Report. South Florida Water Management District, West Palm Beach, FL. 128 pp.

Capece, J.C., K.L. Campbell, and L.B. Baldwin. 1988. Estimating runoff peak rates from flat, high-water-table watersheds. Transactions of the ASAE, 31(1): 74-81.

Capece, J.C., K.L. Campbell, L.B. Baldwin, and K.D. Konyha. 1987. Estimating runoff volumes from flat, high-water-table watersheds. Transactions of the ASAE, 30(5): 1397-1402.

Creasey, C.L. and S.J. Dreiss. 1988. Porous cup samplers: cleaning procedures and potential sample bias from trace element contamination. Soil Science, 145(2): 93-101.

Debyle, N.V., R.W. Hennes, and G.E. Hart. 1988. Evaluation of ceramic cups for determining soil solution chemistry. Soil Science, 146(1): 30-36.

Doolittle, J.A. 1987. Using ground-penetrating radar to increase the quality and efficiency of soil surveys. In: Soil survey techniques, edited by W.U. Reybold and G.W. Anderson. SSSA Special Publication Number 20. Soil Science Society of America, Madison, WI.

England, C.B. 1974. Comments on: A technique using porous cups for water sampling at any depth in the unsaturated zone, by W.W. Wood. Water Resources Research, 10(5): 1049.

Everts, C.J. and R.S. Kanwar. 1990. Estimating preferential flow to a subsurface drain with tracers. Transactions of the ASAE, 33(2): 452-457.

Federico, A.C., K.G. Dickson, C.R. Kratzer, and F.E. Davis. 1981. Lake Okeechobee water quality studies in the Chandler Slough Watershed. Technical Publication 81-2. South Florida Water Management District, West Palm Beach, FL. 270 pp.

Galgowski, C.G. and W.R. Wright. 1980. A variable-depth ground water sampler. Soil Science Society of America Journal, 44: 1120-1121.

Gilley, J.E., S.C. Finkner, J.W. Doran, and E.R. Kottwitz. 1990. Adsorption of bromide tracers onto sediment. Applied Engineering in Agriculture, 6(1): 35-38.

Grossmann, J. and P. Udluft. 1991. The extraction of soil water by the suction-cup method: a review. Journal of Soil Science, 42: 83-93.

Haines, B.L., J.B. Waide, and R.L. Todd. 1982. Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: report of discrepancies. Soil Science Society of America Journal, 46: 658-661.

Hamlett, J.M. 1987. Nitrate movement under a ridge configuration: a field and model investigation. Ph.D. Dissertation. Department of Agricultural Engineering, Iowa State University. Ames, IA.

Hansen, E.A. and A.R. Harris. 1974. A ground water profile sampler. Water Resources Research, 10(2): 375.

Hansen, E.A. and A.R. Harris. 1975. Validity of soil-water samples collected with porous cups. Soil Science Society of America Journal, 39: 528-536.

Harris, A.R. and E.A. Hansen. 1975. A new ceramic cup soil-water sampler. Soil Science Society of America Proceedings, 39: 157-158.

Hughes, S. and B. Reynolds. 1988. Cation exchange properties of porous ceramic cups: implications for field use. Plant and Soil, 109: 141-144.

Kablan, A.T. 1986. Evaluation of selected methods for determining soil hydraulic conductivity. Master's Thesis. Department of Soil and Water Science, University of Florida. Gainesville, FL.

Kanchanasut, P. and D.R. Scotter. 1982. Leaching patterns in soil under pasture and crop. Australian Journal of Soil and Water, 20(3): 193-202.

Klapwijk, A. 1983. Application of denitrification in the wastewater treatment. In: Denitrification in the nitrogen cycle, edited by H.L. Golterman. Plenum Press. New York, NY.

Knighton, M.D. and D.E. Streblow. 1981. A more versatile soil water sampler. Soil Science Society of America Journal, 45: 158-159.

Krajenbrink, G.J.W., D. Ronen, W. van Duijvenbooden, M. Magaritz, and D. Wever. 1988. Monitoring of recharge water quality under woodland. Journal of Hydrology, 98: 83-102.

Lee, Sang-Ill. 1984. Denitrification with wastewater organics. Masters Thesis. Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.

Levin, M.J. and D.R. Jackson. 1977. A comparison of in situ extractors for sampling soil water. Soil Science Society of America Journal, 41: 535-536.

Linden, D.R. 1977. Design, installation, and use of porous ceramic samplers for monitoring soil-water quality. Technical Bulletin 1562. Agricultural Research Service, U. S. Department of Agriculture, Washington, DC. 16 pp.

Litaor, M.J. 1988. Review of soil solution samples. Water Resources Research, 24(5): 727-733.

Marko-Varga, M., G.I. Csiky, and J.A. Jonsson. 1984. Ion chromatographic determination of nitrate and sulfate in natural waters containing humic substances. Analytical Chemistry, 56: 2066-2069.

Metcalf & Eddy, Inc. 1979. Wastewater engineering: treatment, disposal, and reuse, 2nd Edition. McGraw-Hill Book Company. New York, NY.

Mitchell, R. 1974. Introduction to environmental microbiology. Edited by G.H. Sewell. Prentice-Hall, Englewood, NJ.

Morrison, R.D. 1982. A modified vacuum-pressure lysimeter for soil water sampling. Soil Science, 134(3): 206-210.

Morrison, R.D. and J. Szecsody. 1985. Sleeve and casing lysimeters for soil pore water sampling. Soil Science, 139(5): 446-451.

Nagpal, N.K. 1982. Comparison among and evaluation of ceramic porous cup soil water samples for nutrient transport studies. Canadian Journal of Soil Science, 62: 685-694.

Nechamkin, H. 1968. The chemistry of the elements. McGraw Hill, New York, NY. 138 pp.

Nelson, D.W., L.B. Owens, and R.E. Terry. 1973. Denitrification as a pathway for nitrate removal in aquatic systems. Indiana Technical Report 42. Purdue University Water Resources Research Center, West Lafayette, IN. 82 pp.

Nightingale, H.J., D. Harrison, and J.E. Salo. 1985. An evaluation technique for ground water quality beneath urban runoff retention and percolation basins. Ground Water Monitoring Review, 5(1): 43-50.

Nofziger, D.L. 1985. Interactive simulation of one-dimensional water movement in soils: user's guide. Department of Agronomy, Oklahoma State University, Stillwater. 107 pp.

Owen, W.F., D.C. Stuckey, J.B. Healy, L.Y. Young, and P.L. McCarty. 1979. Bioassay for monitoring biochemical methane potential and anaerobic toxicity. Water Research, 13: 485-492.

Owens, L.B., R.W. Van Keuren, and W.M. Edwards. 1985. Groundwater quality changes resulting from a surface bromide application to a pasture. Journal of Environmental Quality, 14(4): 543-548.

Pedersen, J.K., P.L. Bjerg, and T.H. Christensen. 1991. Correlation of nitrate profiles with groundwater and sediment characteristics in a shallow sandy aquifer. Journal of Hydrology, 124: 263-277.

Picken, J.F., J.A. Cherry, G.E. Grisk, W.F. Marritt, and B.A. Risto. 1978. A multilevel device for ground-water sampling and piezometric monitoring. Ground Water, 16(5): 322-327.

Ranson, M.D. and N.E. Smack. 1986. Water table characteristics and water chemistry of seasonally wet soils of Southwestern Ohio. Soil Science Society of America Journal, 50: 1281-1290.

Rasmussen, L., P. Jorgensen, and S. Kruse. 1986. Soil water samples in ion balance studies on acidic forest soils. Bulletin of Environmental Contaminant Toxicology, 36: 563-570.

Rauland-Rasmussen, K. 1989. Aluminum contamination and other changes of acid soil solution isolated by means of porcelain suction-cups. Journal of Soil Science, 40: 95-101.

Reynolds, E.R. 1966. The percolation of rainwater demonstrated by fluorescent dyes. Journal of Soil Science, 17(1): 127-132.

Severson, R.C. and D.F. Grigal. 1976. Soil solution concentrations: effect of extraction time using porous ceramic cups under constant tension. Water Resources Bulletin, 12(6): 1161-1170.

SFWMD. 1980. Engineering hydrology and water quality analysis of detention/retention sites. South Florida Water Management District, West Palm Beach, FL. 99 pp.

Shaffer, K.A., D.D. Fritton, and D.E. Baker. 1979. Drainage water sampling in a wet, dual-pore soil system. Journal of Environmental Quality, 8(2): 241-246.

Silkworth, D.R. and D.F. Grigal. 1981. Field comparison of soil solution samplers. Soil Science Society of America Journal, 45: 440-442.

Smart, P.L. and I.M. Laidlaw. 1977. An evaluation of some fluorescent dyes for water tracing. Water Resources Research, 13(1): 15-33.

Smettem, K.R. and S.T. Trudgill. 1983. An evaluation of some fluorescent and non-fluorescent dyes in the identification of water transmission routes in soils. Journal of Soil Science, 34: 45-56.

Soil Science Department. 1988. Characteristics data for selected Florida soils. Institute of Food and Agricultural Sciences, University of Florida, Gainesville, FL.

Sompongse, D. 1978. Nitrogen cycle studies in Lake Conway. Masters Thesis. Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL.

Sondergaard, M. 1990. Pore water dynamics in the sediment of a shallow and hypertrophic lake. Hydrobiologia, 192: 247-258.

Suarez, D.L. 1986. A soil water extractor that minimizes CO_2 degassing and pH errors. Water Resources Research, 22(6): 876-880.

Suarez, D.L. 1987. Prediction of pH errors in soil-water extractors due to degassing. Soil Science Society of America Journal, 51: 64-67.

Tremwel, T.K. 1992. Field hydrologic and nutrient transport model, FHANTM. Ph.D. Dissertation, Department of Agricultural Engineering, University of Florida, Gainesville, FL. 178 pp.

Trudell, M.R., R.W. Gillham, and J.A. Cherry. 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. Journal of Hydrology, 83: 251-268.

Turner Designs, 1974. Fluorometric facts. Turner Designs, Palo Alto, CA. 20 pp.

USDA-SCS. 1971. Soil survey, Okeechobee County, Florida. U.S. Department of Agriculture, Soil Conservation Service, Washington, D.C.

Van De Pol, R.M., P.J. Wierenga, and D.R. Nielsen. 1977. Solute movement in a field soil. Soil Science Society of America Journal, 41: 10-13.

Van Luik, A. and W. Harrison. 1984. Mined land reclamation using polluted urban navigable waterway sediments: III. Experience at a demonstration site. Journal of Environmental Quality, 13(3): 423-431.

Warrick, A.W. and A. Amoozegar-Fard. 1977. Soil water regimes near porous cup water samplers. Water Resources Research, 13(1): 203-207.

Wood, A.L., J.T. Wilson, R.L. Cosby, A.G. Hornsby, and L.B. Baskin. 1981. Apparatus and procedure for sampling soil profiles for volatile organic compounds. Soil Science Society of America Journal, 45: 442-448.

Wood, W.W. 1973. A technique using porous cups for water sampling at any depth in the unsaturated zone. Water Resources Research, 9(2): 486-488.

Wood, W.W. 1974. Reply to England's comments. Water Resources Research, 10(5): 1050.

Zimmermann, C.F., M.T. Price, and J.R. Montgomery. 1978. A comparison of ceramic and teflon in situ samplers for nutrient pore water determination. Estuarine and Coastal Marine Science, 7: 93-97.

BIOGRAPHICAL SKETCH

John Christopher Capece is a Florida native born in Orlando on August 18, 1960. His father served as a career non-commissioned officer in the U.S. Air Force and the family resided in Virginia, Japan, and Germany between 1961 and 1971. In 1972 the family returned to Florida and settled in Fort Walton Beach. After completing high school, John attended the University of South Florida in Tampa. As a civil engineering student, he worked for the U.S. Geological Survey on various water resource projects. In 1980 he transfer to University of Florida to study agricultural engineering, attracted by its friendly atmosphere, interesting faculty, and progressive educational program.

John completed his Bachelor of Science in Engineering with Honors in 1982. As a research assistant to Dr. Kenneth Campbell, John continued for a Master of Engineering in 1984. His thesis described the development of improved runoff volume and peak rate estimation methods for flatwoods watersheds. Immediately upon completion of his degree, John was assigned to Cameroon, West Africa as a part of a University of Florida technical assistance team. He served as the only American instructor within a very diverse international faculty at the National Advanced School of Agriculture located near Yaounde.

In 1985, John returned to graduate school as a research fellow at Iowa State University. After a year in Iowa, John realized that his true interests and career goals lay in Florida, so he returned to Gainesville in 1986 to begin his doctoral program. In 1987, John's became more involved in student issues and organizations. Along with a handful of students from other universities, John founded the National Association of

Graduate Students. In 1989 he served as its first nationally-elected president. Soon after, John formed the national graduate student honor society, Alpha Epsilon Lambda, as well as other non-profit organizations promoting educational exchanges with China, Russia, and India. Upon completing the degree he plans to begin work as an assistant professor, Water Quality Scientist, at the IFAS Southwest Florida Research and Education Center.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth L. Campbell

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Wendy D. Graham
Assistant Professor of
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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